A study of metal ions in aqueous solution using NMR Spectroscopy

by

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To Mum and Dad

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ABSTRACT

A study was carried out to investigate the properties of certain metal ions in solution using multinuclear magnetic resonance techniques as the mode of analysis.

The majority of this work has involved the collection of numerous chemical shift measurements especially for the lead-207 nucleus and the cadmium-113 nucleus. The data obtained from these experiments have been utilized in several ways. Experiments have shown that the nuclei in different environments behave differently towards concentration and temperature changes. The nuclei investigated also appear to have quite specific characteristic behaviour when attached to different atoms of ligands, for example, the resonance signal for lead-207 attached to oxygen will be different from the lead-207 signal attached to nitrogen. The chemical shift data were also used to calculate some equilibrium constant (K) values using a proposed theoretical model.

Some relaxation time measurements for various lead compounds have been collected in order to further characterise the nature of a particular lead species in solution. The theories involved with relaxation, the mechanisms of relaxation and the practical aspects connected with these experiments have been discussed.

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CHAPTER ONE

THE THEORY OF NUCLEAR MAGNETIC RESONANCE

INTRODUCTION

The study of many elements using NMR techniques has been developed only in recent years due to the widespread use of Fourier Transform Nuclear Magnetic Resonance. Various factors may limit the study. To begin any study there must be a chemical interest in the element, the nucleus must be stable for NMR spectroscopy to be carried out, the nucleus must possess a suitable isotope with a nuclear spin which occurs in a reasonable natural abundance and the nucleus must give a reasonably intense signal.

Nuclei which yield an NMR signal may be grouped in several ways:

a) Spin quantum number, I, $I = \frac{1}{2}$ versus $I > \frac{1}{2}$

b) According to rarity.

c) According to magnetic strength.

1.1 NUCLEI STUDIED BY NMR

There are 24 elements in the periodic table with non-radioactive nuclei with $I = \frac{1}{2}$.

Non metals	H	C	N	F	Si	P	Se	Te	Xe
Main group or Group B metals	Sn	Tl	Pb						
Transition metals	Fe	Y	Rh	Ag	Cd	W	Os	Pt	Hg
Inner transition group metals or lanthanides	Tm	Yb							

Four of the five elements in Group IV have nuclei with $I = \frac{1}{2}$ that are suitable for NMR studies, these are ^{13}C, ^{29}Si, ^{119}Sn and ^{207}Pb.

This situation is unique in the periodic table. A considerable amount of work has been carried out on ^{13}C NMR. ^{29}Si and ^{119}Sn have been investigated quite well, but ^{207}Pb has not been investigated to such an extent. This is probably due to the fact that there is less chemical interest in lead than the other elements of Group IV.

Cadmium, in common with several other elements, has two isotopes with spin-$\frac{1}{2}$, these are ^{113}Cd and ^{111}Cd. ^{113}Cd is considered to be the better isotope for NMR studies because it has a higher receptivity. There is no reason to study the less favourable nucleus, since the primary isotope effects on chemical shifts are generally negligible.

There are six spin-$\frac{1}{2}$ nuclei with about 100% natural abundance; these include ^{1}H and ^{19}F.

There are over 43 quadrupolar nuclei (nuclei with spin $> \frac{1}{2}$) that can be studied, these include ^{35}Cl, ^{33}S. Working with quadrupolar nuclei does present problems, the main one being the very large linewidths which prevent accurate measurements of chemical shifts and the resolution of lines caused by chemically similar sites.

Table 1:1 TABLE OF PROPERTIES OF THE MAGNETIC NUCLEI STUDIED IN THIS THESIS

Isotope	Larmor Frequency in MHz	Natural Abundance %	Magnetogyric Ratio γ (10^7 rad T^{-1} S^{-1})	Spin I	Magnetic Moment μ	Quadrupole Moment $(Q)10^{-28}$ m^2
^{1}H	100.000000	99.985	26.7510	½	4.8371	
^{13}C	25.145004	1.108	6.7263	½	1.2162	
^{19}F	94.093795	100	25.1665	½	4.5506	
^{113}Cd	22.193173	12.26	-5.9330	½	-1.0728	
^{207}Pb	20.920597	22.6	5.5968	½	1.0120	
^{14}N	7.224	99.64	1.9324	1	0.5706	1.6×10^{-2}
^{35}Cl	9.798	75.53	2.6212	$^{3}/_{2}$	1.0598	-7.89×10^{-2}
^{33}S	7.670	0.76	2.0517	$^{3}/_{2}$	0.8296	-6.4×10^{-2}

1.2 The History of the Development of Nuclear Magnetic Resonance (NMR) Spectroscopy

Nuclear Magnetic Resonance is used to study the magnetic properties of the nucleus in the presence of an external magnetic field. In practice NMR has a range of radiation between 2 and 100 x 10^6 Hz, which relative to Infra Red spectroscopy, with a range of 10^{12} to 10^{15} Hz and Ultra Violet with a range of 10^{15} to 10^{18} Hz, is relatively narrow.

The fact that nuclei have magnetic properties was first discovered during the study of optical spectroscopy. Once spectrographs with high resolving power were used, hyperfine splitting was observed in the spectra. The very small splittings of certain atomic spectral lines, allowed the indirect observation of angular momentum and magnetic moments. This study led Pauli[1] in 1924 to suggest that certain nuclei had angular momentum and hence a magnetic moment.

In the early 1920's Stern[2] and Gerlach showed that a beam of atoms passed through an inhomogeneous magnetic field deflected according to the orientation of the electron magnetic moment relative to the magnetic field. During the 1930's this technique was improved and the smaller values of nuclear magnetic moments could be measured.

In 1946 nuclear magnetic resonance was observed in bulk matter (liquids or solids) by two separate teams of physicists. Purcell, Torrey and Pound[3], at Harvard University, used a single coil probe and detected the proton magnetic absorption signal of a piece of paraffin wax at 30 MHz. Bloch, Hansen and Packard[4] detected a magnetic induction signal from the protons of water at 7.765 MHz, using a crossed coil probe, at Stanford University. Bloch and Purcell shared the Nobel Prize awarded in 1952 for Physics for their discoveries.

At this stage, NMR was used only to determine the nuclear magnetic moments of nuclei.

In 1949, Knight[5] first observed a phenomenon known later as chemical shift. After 1950 it became apparent that the precise resonance frequency of a nucleus depended upon the state of the chemical environment. This meant that NMR could be a very useful technique for chemists.

In 1951[6] separate resonance lines were found for different protons of the same molecule, so NMR could be used as a probe for the structure of a molecule.

The first commercial NMR instrument became available in 1956.

Experiments in the 1950's were mainly concerned with proton studies. Metal elements only really started to be investigated during the 1960's when internuclear double resonance techniques (INDOR) were used.

Until 1966, high resolution NMR spectra were obtained by sweep techniques by either sweeping the radio frequency or the magnetic field[7]. In 1966, Ernst and Anderson[8] showed that using Fourier transform (FT) techniques for high resolution NMR was a more efficient way of obtaining spectra. At first FT techniques were expensive, as an extra piece of equipment was needed to modify an existing spectrometer. Now, FT techniques are cheaper as special instruments have been built to observe resonance with a wide range of nuclei.

1.3 Fourier Transform Spectroscopy

The Fourier transform is a general mathematical transform developed by Baron Jean Baptiste Joseph Fourier, which relates important pairs of physical variables[9]. The transform is used to relate time and frequency in FTNMR. Experimental results are obtained in the time domain and then transformed to the frequency domain. This can be represented simply by the expression:

$$F(\omega) = \int_{-\infty}^{+\infty} f(t)\, e^{-i\omega t}\, dt$$

where ω = frequency

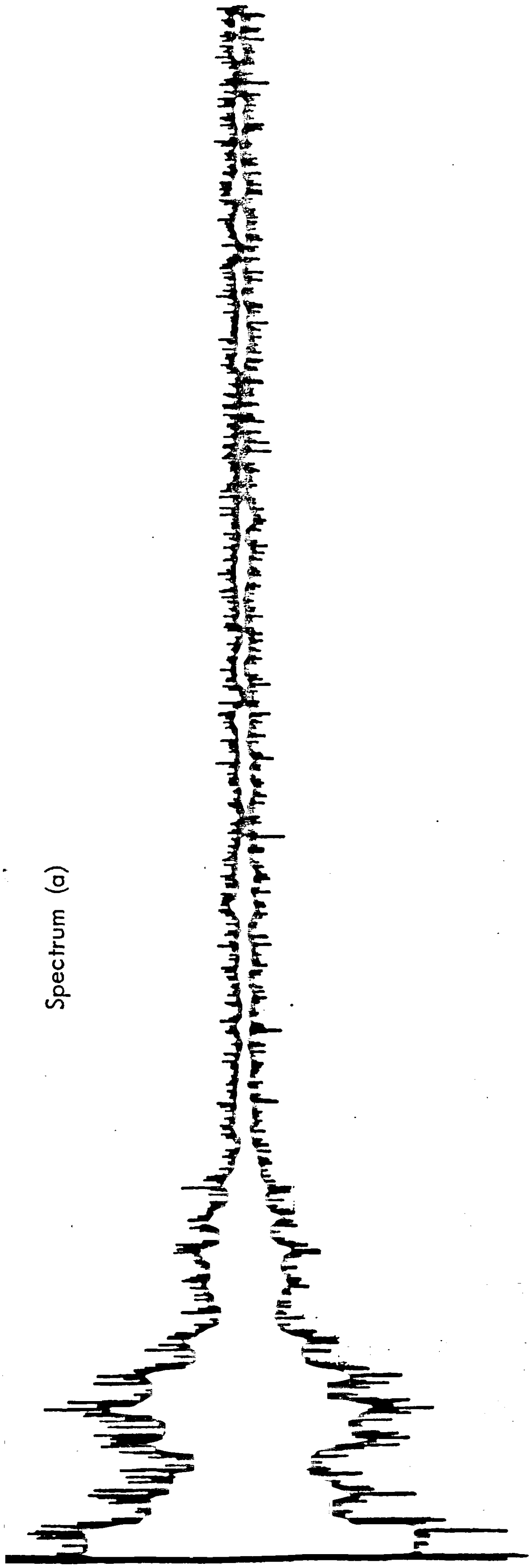
t = time

The results obtained in the time domain are stored in the spectrometer's computer and yield a spectrum known as the Free Induction Decay curve (FID), see spectrum (a). The FID is then transformed to give a normal or frequency domain spectrum. Spectrum (b) is the transformed spectrum of (a). The actual transform is accomplished using the Cooley Tukey fast Fourier transform algorithm[10]. This method is a shorter procedure as regards computer time and uses less memory than the basic FT method.

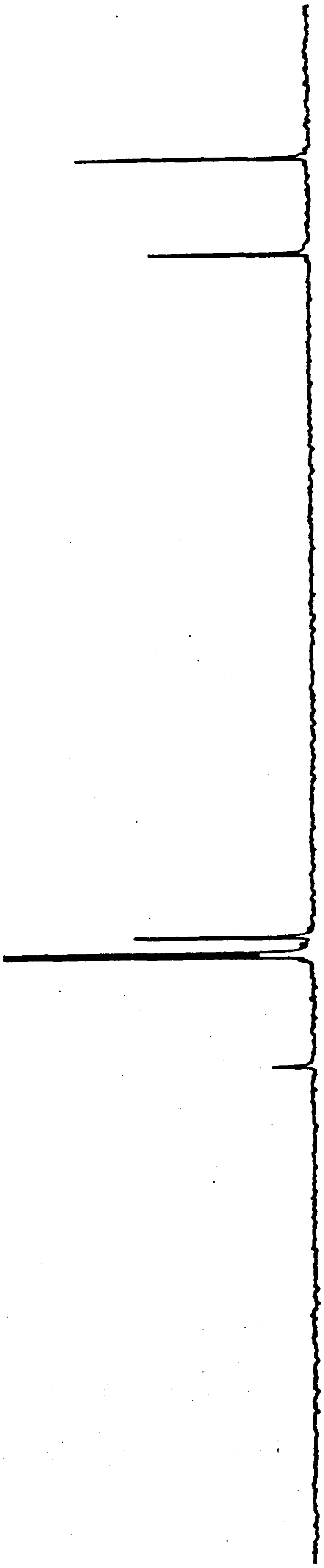
The following ^{13}C spectra of ethyl benzene were obtained on the Jeol FX90Q spectrometer.

Spectrum (a) shows the FID

Spectrum (b) shows the transformed FID



Spectrum (a)



Spectrum (b)

1.4 The Principles of Magnetic Resonance

NMR absorption occurs when certain nuclei are subjected to radiofrequency in a strong magnetic field. Only nuclei with spin angular momentum, $I \geq \frac{1}{2}$ and a non-zero magnetic moment, μ, will undergo absorption. This means that NMR spectra of nuclei such as ^{1}H, ^{19}F, ^{31}P can be obtained, but spectra of nuclei such as ^{12}C, ^{16}O, ^{32}S cannot be obtained.

Nuclei may be divided into three principal groups according to their spin angular momentum values:

Group 1) $I = 0, \mu = 0$ e.g. $^{12}_{6}C$

Group 2) $I = \frac{1}{2}, \mu > 0$ e.g. $^{207}_{82}Pb$

Group 3) $I > \frac{1}{2}, \mu > 0$ $Q > 0$ e.g. $^{2}_{1}H$
(where Q = Electric Quadrupole moment)

A fundamental quantum law states that in a uniform magnetic field, a nucleus with spin quantum number, I, can assume $2I + 1$ orientations.

Therefore when $I = \frac{1}{2}$, the number of possible orientations is 2.

Nuclear magnetic moments are often expressed in terms of a constant, known as the magnetogyric ratio,

$$\gamma = \mu / P \qquad \text{Equation 1}$$

where P = spin angular momentum.

The SI units for γ are: rad T^{-1} S^{-1} and for nuclei with $I = \frac{1}{2}$, known values range from 28.5335×10^{7} rad T^{-1} S^{-1} for ^{3}H, to -20.378×10^{7} rad T^{-1} S^{-1} for ^{3}He. γ is characteristic of a particular nucleus and may be positive or negative.

It is quite useful to describe the equations used in pulsed NMR experiments in terms of the laws of classical mechanics and in terms of quantum mechanics. The classical method will be discussed here more fully, as it gives a better explanation for pulsed NMR and relaxation effects than the quantum mechanics approach. The quantum mechanical approach involves some complicated mathematical treatments and is really more suited to explain spectral analysis problems.

1.5 The Classical Mechanical Theory

The nucleus under observation is placed in a magnetic field of flux density B_0. The magnetic moment, μ , experiences a torque which may be represented as a vector product of μ and B_0. The following equation can then be written from Newton's Laws of Motion:

$$\frac{d\underline{P}}{dt} = \underline{\mu} \times \underline{B}_0 \qquad \text{Equation 2}$$

The nucleus in the magnetic field will align itself with respect to the field, and will precess at an angle, θ , about the field. The precession is known as the Larmor Precession.

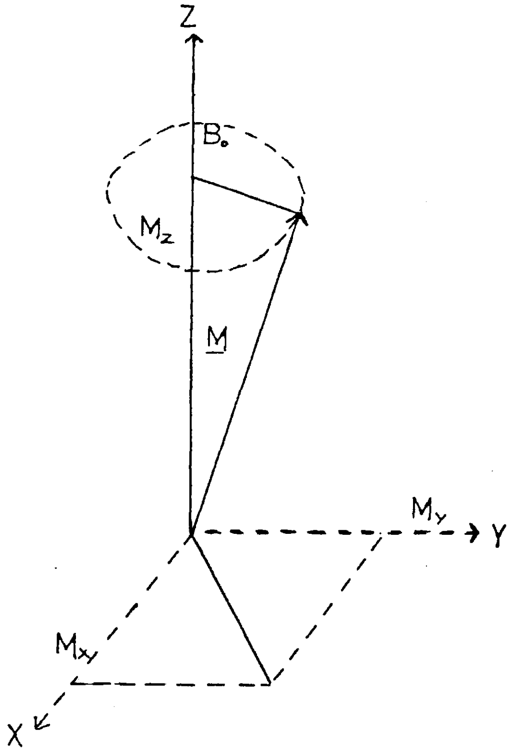


Diagram 1 shows the precession of a nuclear magnetic moment, in a magnetic field, B_0, for $\gamma > 0$ [129]

For angular motion with velocity ω_0, the rate of change of angular momentum is given by: $P\omega_0$

Equation 3 $\frac{d\underline{P}}{dt} = \underline{P}\,\omega_0$ and $P\,\omega_0 = \mu\, B_0$ Equation 4 then from equation 1:

$$\omega_0 = \gamma B_0$$

or Equation 5

$$\nu_0 = \gamma B_0$$

Equation 5 is a very fundamental equation. It is known as the Larmor Equation and describes the basic phenomenon of nuclear magnetic resonance.

The classical theory does not give any information about which transition probabilities are to be expected, or how the excitation energy should be applied. Quantum mechanics describes these quantities.

The absorption of energy by the nuclei concerned can be regarded as a resonance phenomenon. It has already been stated that the nuclei precess about the magnetic field at the Larmor frequency (Equation 5). The nuclei are excited by applying a small magnetic field, B_1, about the basic field, B_0 (conventionally placed along the Z axis). When the rotation frequency of B_1 is equal to ν_0 , and in the same sense, resonance will occur. This means that energy will be absorbed from the exciting field, which will result in the nuclei precessing around B_0 at a bigger value of θ than the equilibrium θ value. The measured absorption of energy from the exciting field is the Larmor condition.

1.6 The Quantum Mechanical Theory

This theory supposes that the spin angular momentum of a nucleus must be quantised. If the quantum number is referred to as I , the angular momentum P, of the nucleus may be written as[11]:

$$P=[I(I+1)]^{\frac{1}{2}}\frac{h}{2\pi}$$

The observable magnitudes of the magnetic moment along the Z axis can be expressed in terms of a magnetic quantum number, m.

$$P_z = m_I\hbar \qquad \text{where} \quad m_I = I, (I-1), (I-2)\ldots -I$$

Changes in P_z are subject to the selection rule that $\Delta m = \pm 1$.

If $I = \frac{1}{2}$ there are two possible values of m_I; $\pm\frac{1}{2}$, and two possible values of P.

When a nucleus is placed in a magnetic field, B_o, the Hamiltonian Operator, $\hat{\mathcal{H}}$, can be considered. Where

$$\hat{\mathcal{H}} = -\hat{\underline{\mu}}_z\underline{B}_o$$

Rewriting Equation 1 to include $\hat{\mathcal{H}}$

$$\hat{\mathcal{H}} = -\gamma\hbar\hat{I}_zB_z$$

The allowed energy levels for the system become

$$E=-\gamma h m B_o$$

For nuclei with $I = \frac{1}{2}$, there are two energy levels which correspond to $m = \pm\frac{1}{2}$. The separation between the energy levels can be written as:

$$\Delta E=\gamma h B_o = \frac{\mu B_o}{I}$$

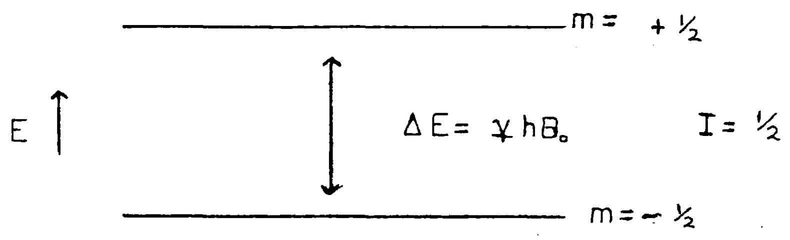


Diagram 2: The separation between energy levels.

If some energy is provided which is equal to the energy difference between the two levels, then energy will be absorbed and by Planck's Law, the same equation as in the classical approach (equation 5) is found for the absorption of energy by the nuclear spins.

Therefore classical and quantum theory approaches both reach the same resonance condition conclusion.

The theories used so far have considered only how a single isolated nuclear spin would behave under certain conditions. When an NMR spectrum is measured, the mean behaviour of a lot of similar nuclei is recorded. At thermal equilibrium, the nuclei will be found spread over various energy levels according to the Boltzmann distribution law.

For nuclei of spin quantum number $I = \frac{1}{2}$, there are two possible energy levels; the numbers of nuclei in these levels may be represented as n_u (upper level) and n_l (lower level). The ratio of n_u to n_l may be expressed as a function of the absolute temperature.

$$\frac{n_l}{n_u} = \exp\left(\frac{2\mu B_0}{kT}\right) \simeq 1 + \frac{2\mu B_0}{kT}$$

Where k = Boltzmann constant

T = absolute temperature

(This approximation is possible because the exponent term in the exponential is very small.)

At room temperature, the populations of the spin states are almost equal. From simple calculations, it can be shown that on average, where N is the total number of nuclei:

$$\text{POPULATION OF LOWER STATE} = 1/2\, N\left(1 + \frac{\mu}{kT}\right)$$

$$\text{POPULATION OF UPPER STATE} = 1/2\, N\left(1 - \frac{\mu}{kT}\right)$$

An absorption signal therefore can only arise from a difference between the values of n_u and n_l (the Boltzmann excess). Generally for NMR experiments one nucleus in about 100,000 may lead to a signal.

The magnetic moment can be expressed in terms of a bulk magnetic susceptibility (χ).

$$M = \chi B_0 = \frac{N\mu^2 B_0}{kT}$$

For nuclei with $I = \frac{1}{2}$, the magnetic susceptibility is given by:

$$\chi = \frac{N\mu^2}{kT} = \frac{N\gamma^2 h^2}{4kT}$$

where M = total magnetic moment resolved along the field direction.

The lifetime which a nucleus may spend in an excited state in NMR spectroscopy is relatively long (seconds) in comparison to optical spectroscopy. This has two important results. The first result, due to the uncertainty principle is that as the lifetime is long, the NMR line can be sharp. The second result is that a phenomenon known as saturation may occur. This happens when relaxation from the excited state is slow and a dynamic equilibrium is set up with a strong exciting field. The numbers of nuclei in the upper and lower states of dynamic equilibrium are equal and so the signal saturates, or vanishes.

As NMR experiments never deal with a single nucleus, it is useful to define a macroscopic magnetisation, M, as a vector sum of the individual magnetic moments.

Bloch[7] derived a series of equations which accounted for the behaviour of M in the presence of a radio frequency field.

1.7 The Bloch Equations

These equations are extremely complex and can only really be solved under various limiting conditions, the most useful one being the steady state condition[21].

The full Bloch equations are:

$$\frac{dM_x}{dt} = \gamma\,[M_y B_z - M_z B_1 \sin 2\pi\nu t] - \frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = -\gamma\,[M_x B_z - M_z B_1 \cos 2\pi\nu t] - \frac{M_y}{T_2}$$

$$\frac{dM_z}{dt} = -\gamma\,[M_x B_1 \sin 2\pi\nu t + M_y B_1 \cos 2\pi\nu t] - \left(\frac{M_z - M_0}{T_1}\right)$$

The equations split the total magnetic moment per unit volume M_0, into three components M_x, M_y and M_z and take into consideration the time constants T_1 and T_2 which return the components after a perturbation to their equilibrium values.

1.8 NMR Parameters

NMR experiments can be used to determine five parameters:

1) Chemical shift, δ

2) Coupling constants, J

3) Line intensities

4) Spin lattice relaxation time, T_1

5) Spin-spin relaxation time, T_2

The first three parameters lead to structural information, while the last two parameters lead to information about molecular motion.

1.9 The Chemical Shift and the problems with referencing

This is the most important, single parameter to be derived from an NMR experiment. The chemical shift is determined by the environment of the nucleus and it may either refer to changes in resonance (Larmor) frequency or changes in shielding (screening)[12].

Since at constant B_o

$$(\nu_A - \nu_B) \; \alpha - (\sigma_A - \sigma_B)$$

where σ = shielding
A = nucleus A
B = nucleus B
ν = resonance frequency

increasing the resonance frequency, implies a decrease in the shielding value.

The chemical shift is usually measured with respect to a particular signal, and is given the symbol δ, with units of parts per million (ppm) as recommended by IUPAC[13]. By convention, δ is said to increase with increasing frequency[14] and may be expressed as:

$$\delta_x = \frac{\nu_x - \nu_{reference}}{\nu_{reference}} \times 10^6 \qquad \text{ppm}$$

where x refers to the sample

ν refers to the resonance frequency

A positive value of δ_x indicates that the nuclei of x resonate at a higher frequency (lower field) than the reference compound.

To quote shifts in ppm, a suitable reference compound has to be found. A reference may be an internal reference, or an external reference. If it is an internal reference, a small amount (ca. 5%) of the compound is added to the sample and solvent in the NMR tube. If the reference is external, there are either two NMR tubes, e.g. 8mm inside a 10mm tube, with the reference in the outer tube and the sample in the inner tube, or, an inner capillary containing the reference inside the sample tube, so that the sample and reference are maintained separate.

For ^{1}H, ^{13}C and ^{29}Si, tetramethylsilane (TMS) is used as an internal reference. Other nuclei present problems, because choosing a reference compound for them is extremely difficult. When choosing a reference compound the following considerations must be taken into account. For an ideal reference compound, there should only be one resonance signal for the observed nucleus, the substance should be chemically inert and it should give an intense signal away from the signal(s) of the sample compound.

When an internal reference is used, the magnetic susceptibility effects are the same for the standard molecules as the sample molecules, so the value of B_0 is the same for both.

Problems arising from referencing may be reduced by using an external reference, although corrections then have to be made for bulk susceptibility[15,16].

Measurements with external standards in cases of known chemical shifts, may be used in an NMR method of obtaining magnetic susceptibilities.

When no suitable reference compound can be found, the locking material used to stabilise the magnetic field may be used as a reference. When this happens, the reference material is referred to as a second order reference.

Under ideal conditions, chemical shifts should be reported for infinite dilution in an inert solvent. These conditions seldom occur as there are interactions (weak or otherwise) with the solvent, so there will be small changes in the chemical shift values. The changes are difficult to predict and they affect the accuracy of any measurement by an unknown amount. The overall shift may be shown by a five-term equation.

$$\delta_S = \delta_B + \delta_A + \delta_E + \delta_H + \delta_W$$

where: S = Solvent

B = Bulk susceptibility

A = Anisotropy contribution

E = Reaction Field

H = H-bonding and interactions

W = Van der Waal contributions

Another method of referencing is known as substitution. The sample and standards are placed in separate tubes of the same size. The spectrum of each is then recorded in the order, standard, sample, standard. This sequence allows for any drift in the field between the measurements. This method is only really used for weak samples of the more difficult to observe nuclei.

Theoretically in all cases, it would be better to reference measurements to the appropriate bare nucleus.

Chemical shifts can also be defined in terms of a shielding constant;

$$\delta = \sigma - \sigma_r$$

where σ = shielding constant of observed nucleus

σ_r = shielding constant of the reference nucleus

1.10 Shielding constant (also known as the screening constant)

This constant varies with the type and number of ligands attached to the nucleus.

The shielding constant for molecules, from Ramsey's[17] theory may be given as;

$$\sigma = \sigma_d + \sigma_p$$

where d = diamagnetic term

p = paramagnetic term

Evaluation of, σ, requires a detailed knowledge of wave functions for excited states and the information is rarely available.

The diamagnetic and paramagnetic terms differ for different nuclei in the same molecule[18], due to an uneven distribution of electron density.

The shielding of an ion has been interpreted by several methods[19]. It has been proposed for example that there are different distances of closest approach between an ion and the solvent, due to the different strengths of the hydrogen bonds formed by D_2O and H_2O.

1.11 Coupling Constant

These values may be either positive or negative, and may be represented by the term J. Coupling constants are proportional to the product of the relevant magnetogyric ratios.

1.12 Line Intensities

Measurements of line intensities may be important when comparing lines obtained in different spectra, under similar conditions.

1.13 Relaxation Effects

From the early stages in the development of NMR spectroscopy, it was noted that the absorption and emission processes at nuclear resonance frequencies were quite similar. This meant that the observation of signals leads to the fact that some energy has been given to nuclei via an NMR absorption. So there must be pathways by which the nuclear spins can relax toward a lower energy level, i.e. processes where the magnetic energy associated with the spin when it is in the applied field, can be converted into some other form of energy. The other form of energy is eventually usually thermal energy of motion of molecules. This idea led to the concept of spin-lattice relaxation T_1.

If an exchange of energy between two spin systems occurs, i.e. between the spin energised in the NMR absorption process and the neighbouring nuclei possessing a magnetic moment, then the associated relaxation time is known as the spin-spin relaxation time, T_2.

T_1 and T_2 will be discussed later in more detail.

CHAPTER TWO

RELAXATION TIMES

Introduction

The study of relaxation times, T_1 and T_2, of individual lines of a high resolution spectrum was originally proposed in 1968,[20] when Fourier Transform techniques became available.

Relaxation processes take place via interactions between nuclei and locally fluctuating magnetic fields (and electric fields where quadrupolar nuclei are concerned). These processes yield valuable information about molecular motion and the stereochemistry of the systems under investigation.

The processes are first order exponential reactions, with the relaxation times being the time constant for the decay. T_1 and T_2 describe the return to equilibrium of the nuclear magnetisation.

T_1 is referred to as the longitudinal, or spin-lattice relaxation time, which is an energy effect that shows the rate of transfer of energy from the nuclear spin system to its surrounding environment.

T_2 is referred to as the transverse, or spin-spin relaxation time; it is an entropy effect which involves the rate of decay of the transverse magnetisation.

In a non-viscous liquid T_1 is often equal to T_2, but T_2 may be shortened by chemical exchange, interaction with a paramagnetic centre or scalar coupling with a quadrupolar nucleus.

There are six main mechanisms that may affect the relaxation processes. These are:- scalar coupling, spin rotation, dipole-dipole interactions, a quadrupolar mechanism, chemical shift anisotropy and paramagnetic contributions.

2.1 Scalar Coupling ($T_{1,2}^{SC}$)

This mechanism is important when an observed spin, I, is coupled with a spin, S. When two such nuclei are spin coupled the value of the scalar spin-spin coupling constant, J, measures the size of the magnetic field at the nucleus with spin, I, arising from the spin orientation of S. I will therefore experience changes if S relaxes or J changes.

The equations for scalar coupling can be represented[21] simply by:-

$$\frac{1}{T_1^{SC}} = \frac{8\pi^2 J^2 S(S+1)}{3}\left[\frac{\tau_e}{1+4\pi^2(\nu_I-\nu_S)^2\tau_e^2}\right]$$

$$\frac{1}{T_2^{SC}} = 4\pi^2 J^2 S(S+1)\left[\tau_e \quad \frac{1}{1+4\pi^2(\nu_I-\nu_S)^2\tau_e^2}\right]$$

where S = spin of the quadrupolar nucleus

τ_e = exchange lifetime

ν_I, ν_S = Larmor frequencies of the two nuclei involved

J = scalar spin-spin coupling constant

2.2 Spin Rotation ($T_{1,2}^{SR}$)

This mechanism occurs when there is an interaction between the nuclear magnetic moment and the fluctuating magnetic fields which are generated by the molecular magnetic moment associated with the charge distribution within the molecule. This term is directly proportional to the temperature of the system.[22]

Relaxation due to spin rotation is particularly effective at high temperatures due to the molecule increasing its rate of rotation with temperature.

Small molecules, molecules relaxing in the gas phase, and nuclei with large chemical shift ranges appear to relax preferentially by this mechanism.

Nuclei that are partially relaxed by this mechanism show a non-linear behaviour in T_1 values as a function of temperature. When other relaxation mechanisms are contributing to the overall T_1 value, the contribution due to spin rotation may be detected via the temperature relationship.

For liquids undergoing isotropic molecular rearrangement the spin rotation relaxation rate may be given by

$$\frac{1}{T_1^{SR}} = \left(\frac{2IkT}{3\hbar^2}\right)\left(2C_\perp^2 + C_\parallel^2\right)\tau_J$$

k = Boltzmann's constant

where: $C_\parallel, C_\perp$ = spin rotation coupling constant tensor elements

I = moment of inertia of the molecule

τ_J = correlation time for molecular angular momentum vector. This measures the time a molecule spends in a given angular momentum state.

$\hbar$ = 'reduced' Planck's constant

2.3 Dipole-Dipole ($T_{1,2}^{D-D}$)

This mechanism gives information about overall molecular rotation and is frequency-independent under certain conditions.

For molecules where the magnetic nuclei are in random rapid motion the following equation may be applied:-

$$\frac{1}{T_1^{D-D}} = \frac{1}{T_2^{DD}} = \frac{4\gamma_i^2\ \gamma_J \hbar^2 S(S+1)\tau_c}{3r_{ij}^6}$$

where: τ_c = correlation time

γ = nuclear magnetogyric ratio

r_{ij} = magnitude of vector joining i j

Nuclei i and j can be in the same molecule (intramolecular interactions) when they will move together relative ~~to~~ the direction of B_0 via molecular rotation. Such results must therefore be interpreted in terms of a rotational correlation time. The other situation to be considered in dipole-dipole relaxation is when the nuclei concerned are from different molecules (intermolecular interactions). In this case the nuclei move when the molecules experience translational motion, so these results must be treated in terms of translational correlation times.

2.4 Quadrupolar Relaxation ($T_{1,2}^{Q}$)

This mechanism is important for nuclei with $I > \frac{1}{2}$. Such nuclei have a fluctuating electric field, in addition to the magnetic field, by which relaxation may occur. Normally, if this mechanism is present, it is the dominant relaxation process.

Under simplified conditions:

$$\frac{1}{T_1^{Q}} = \frac{1}{T_2^{Q}} = \frac{3}{40}\left(\frac{2I+3}{I^2(2I-1)}\right)\left(\frac{e^2qQ}{\hbar}\right)^2 \tau_c$$

where: I = spin Quantum number

$\frac{e^2qQ}{\hbar}$ = quadrupolar coupling constant, which is zero in a highly symmetric situation.

Generally relaxation times of quadrupolar nuclei are short. T_1^Q depends on the rotational correlation time; therefore its relationship to temperature and viscosity will be the same as for T_1^{D-D}.

2.5 Paramagnetic contribution $(T_{1,2}^{PARA})$

This term dominates the relaxation of paramagnetic substances. The unpaired electrons present in these substances will generate a local magnetic field and provide a relaxation mechanism[24]. The magnetic moment of an electron is greater than the magnetic moment of a nucleus, so any paramagnetic substances present will contribute significantly to the T_1 value when investigating a process for a diamagnetic substance relaxation.

The basic equations for relaxation by a paramagnetic agent have been devised by Solomon[25] and Bloembergen[26]. The following equations show the term under simplified conditions. They contain terms similar to the ones used for dipolar relaxation and scalar coupling.

$$\frac{1}{T_1^{PARA}} = (4S(S+1)\,\gamma^2\,\gamma_i^2/3\hbar^2 r^6)\,\tau_c$$

$$\frac{1}{T_2^{PARA}} = \frac{1}{T_1^{PARA}} + (S(S+1)\,\alpha^2/\hbar^2)\,\tau_c$$

where: $\propto$ = hyperfine electronuclear spin coupling constant

2.6 Chemical Shift Anisotropy ($T_{1,2}^{CSA}$)

Chemical Shift Anisotropy can be important when the molecule under investigation is non-symmetric and there is a large range in the values of the chemical shift.

The mechanism has a rate which is dependent upon the square of the operating field,[21] and can be represented simply by:

$$\frac{1}{T_1^{CSA}} = \frac{2}{15} \gamma^2 B_0^2 (\Delta\sigma)^2 \tau_c$$

where: $\Delta\sigma$ = chemical shift anisotropy

Bo = static magnetic field of an NMR spectrometer

$T_2 = {}^6/_7\, T_1$

2.7 Overall Relaxation Mechanism ($T_{1,2}^{OBS}$)

The observed relaxation rate, ($R_{1,2}^{OBS}$), or the observed relaxation time ($T_{1,2}^{OBS}$) is the resultant of the various contributory relaxation mechanisms.

$$(R_{1,2}^{OBS}) = \frac{1}{(T_{1,2}^{OBS})}$$

$R_{1,2}^{OBS}$ is obviously the sum of the rates from contributing mechanisms.

$$R_{1,2}^{OBS} = R_{1,2}^{D-D} + R_{1,2}^{SC} + R_{1,2}^{SR} + R_{1,2}^{CSA} + R_{1,2}^{Q} + R_{1,2}^{PARA}$$

2.8 Mechanisms accounting for $(T_{1,2}^{OBS})$

From knowledge of the chemistry of the system under investigation the probable relevant relaxation mechanisms can be deduced.

Usually, it is a known fact, whether or not paramagnetic or quadrupolar mechanisms are present. If either of these mechanisms is present, then in most cases it will be the most likely source of relaxation.

Scalar coupling is only important in a few cases (and varies as a function of the inverse square of the external field) so normally it is considered to be absent. One such case where it is important is in PBr_3[27]. The ^{79}Br and ^{81}Br nuclei are reported to induce the scalar coupling mechanism along with the spin rotation mechanism.

The dipolar contribution can then be distinguished from the spin-rotation and chemical shift anisotropy contributions, by measuring the nuclear Overhauser effect enhancement (NOE):

$$\eta = \frac{\eta_{max}\, T_1}{T_1^{D-D}}$$

where: η = experimental NOE

η_{max} = maximum NOE obtainable

T_1 = measured spin-lattice relaxation time

The overall relaxation time can then be split into the contribution due to the dipolar mechanism (T_1^{D-D}) and the contributions due to other factors (T_1^{OTHER}):

$$(T_1^{OBS})^{-1} = (T_1^{D-D})^{-1} + (T_1^{OTHER})^{-1}$$

The relaxation due to chemical shift anisotropy can be found by measuring the relaxation time of a particular sample at different magnetic field strengths. From these data a value for, $\Delta\sigma$, the screening anisotropy, can be obtained.

A value due to spin rotation can then be found, by:-

$$(T_1^{\text{OTHER}})^{-1} = \frac{1}{T_1^{\text{SR}}} + \left(\frac{\mu}{15\pi}\right) \gamma_i^2 B_0^2 \Delta\sigma^2 \tau_c$$

and noting the temperature dependence of T_1^{OBS}, as T_1 for this mechanism increases with increasing temperature and is field independent.

2.9 Measurement of T_1

The methods used to measure T_1 require special pulse sequences.

There are three commonly used sequences for T_1 determinations:-

a) Inversion Recovery

b) Saturation Recovery

c) Progressive Saturation

2.10 Inversion Recovery

The method in its most basic form (there are modifications available) uses a pulse sequence:-

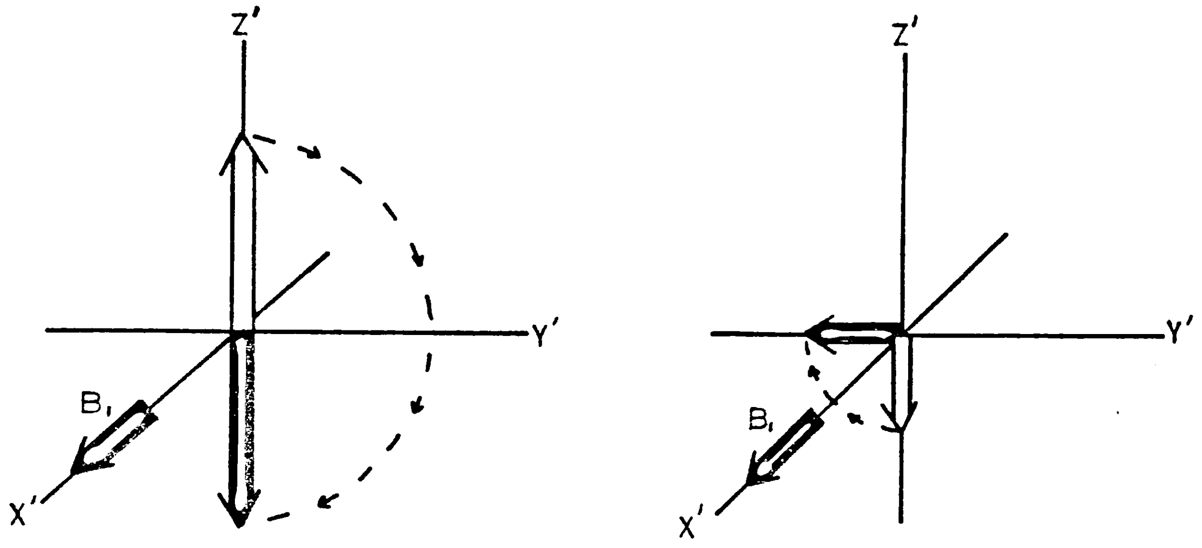
$$180^\circ, \quad \tau \quad , \quad 90^\circ$$

A 180° pulse inverts the spin population, which results in rotating the equilibrium magnetisation to the negative Z axis. The magnetisation is then allowed to relax back towards equilibrium via an exponential process with a rate constant, T_1. After a time, τ , the sample is given a 90°

pulse. This rotates the residual longitudinal magnetisation to the y-axis. See Fig. 2.1.

The resulting Free Induction Decay curve (FID) is stored and a time of at least $5T_1$ is allowed to elapse before repeating the pulse sequence. The sequence is repeated until a good signal to noise ratio is obtained on a transformed spectrum.

About ten different values of τ are needed to obtain a reasonable T_1 value. For τ values that are much less than T_1, the transformed spectrum obtained appears as a negative signal. When $\tau = \ln 2 T_1$, no signal is obtained. When τ is $5T_1$, the signal is positive with an intensity equal to the intensity of a spectrum, i.e. as if only a 90° pulse had been given.

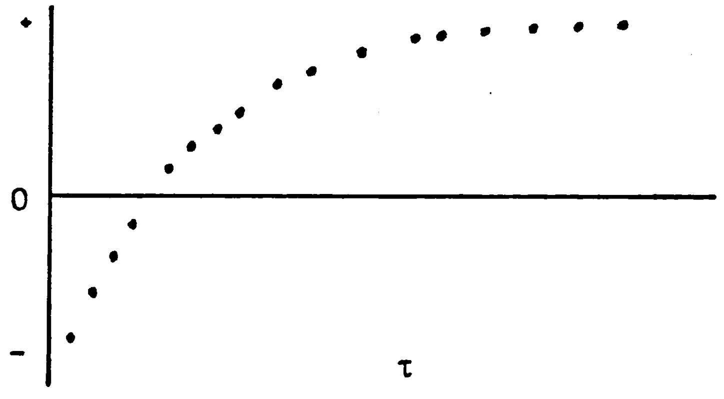


(a)

M is inverted by 180° pulse at Time 0

(b)

After time interval τ , a 90° pulse rotates the remaining M to the -y' axis



(c)

Initial amplitude of the FID as a function of τ

Figure 2.1

2.11 Saturation Recovery

This method uses a 90°, τ , 90° pulse sequence. T_1 is obtained via the measurement of the recovery of the spin system from saturation. The system can be saturated by using a 90° pulse, (with a homogeneity spoiling pulse), or by using five to ten closely spaced 90° pulses. The system is then allowed a time, τ , to return to equilibrium before another 90° pulse is given. The resulting FID is stored, and the sequence is repeated until a spectrum with a reasonable signal to noise ratio is obtained. Various sets of data are then collected with varying τ values, and T_1 can then be calculated.

2.12 Progressive Saturation

This method uses the line intensities of a spectrum as a function of the interval between the 90° pulses to calculate a T_1 value.

2.13 Reasons for using a particular method

There are various advantages and disadvantages attached to the different methods of measuring T_1. The following table summarises these. Table 2.1.

2.14 Advantages and disadvantages of the various methods

TABLE 2.1

SEQUENCE	ADVANTAGES	DISADVANTAGES
a) Inversion Recovery	1. Covers all ranges of T_1 measurements. 2. Insensitive to accuracy of pulses. 3. Quick and easy information obtained about T_1.	1. A prior knowledge of T_1 is needed to set the delay between pulses. 2. Sensitive to off-resonance effects. 3. Requires a 180° pulse.
b) Saturation Recovery	1. Very good sensitivity on long T_1 values. 2. Requires only a 90° pulse.	1. Requires extra hardware. 2. It can interfere with the field-frequency lock autoshim operation.
c) Progressive Saturation	1. More efficient for longer runs. 2. Requires only a 90° pulse. 3. Works on any basic spectrometer.	1. Sensitive to accuracy of 90° pulse. 2. Not applicable to short T_1 values where $T_1 > T_2$

Some errors may be encountered when T_1 measurements are carried out. These errors may arise from either chemical or mechanical interference.

2.15 Examples of Chemical Interference

1. Paramagnetic impurities; from nickel spatula, dissolved oxygen, ions from glassware.
2. Concentration and solvent effects.
3. Molecular diffusion.

2.16 Examples of Mechanical Interference

1. Inaccurate 90° pulse generation.
2. Temperature regulation failure.
3. Stability of spectrometer.
4. Choice of pulse sequence.
5. Method of calculation.[28]
6. Changes in resolution/sensitivity particularly over long periods.

2.17 Measurement of T_2

T_2 is more difficult to measure than T_1 due to the sensitivity of T_2 to low magnetic fields (i.e. sensitive to any inhomogeneity in Bo).

An excellent method was proposed by Hahn[29] to overcome the inhomogeneity problem. This technique was called the spin-echo method.

The spin-echo method consists of a $90^\circ\ \tau\ 180^\circ$ pulse sequence, and the observation at a time 2τ of the Free Induction echo.

The Hahn method has been modified by Carr and Purcell[30] and the Carr-Purcell method has been modified by Meiboom and Gill.[31]

The first modification is to overcome the unwanted effects of a value known as T_2^1. Any inhomogeneity in the basic magnetic field results in a T_2 value modified by the T_2^1 value, so the normally observed value, T_2^* can be written as:-

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2^1}$$

T_2^* can be measured or estimated directly from any spectrum as the linewidth at half height of the NMR line:

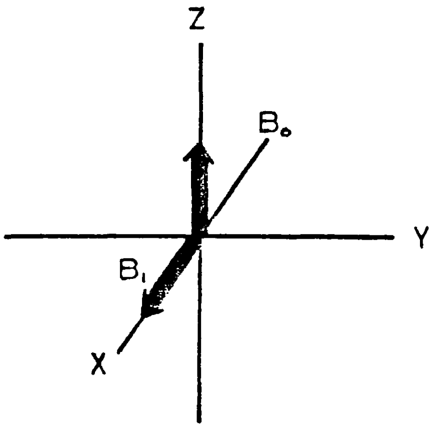
$$T_2^* = \frac{1}{\pi \upsilon_{\frac{1}{2}}} \qquad \text{where} \quad \upsilon_{\frac{1}{2}} = \text{linewidth at half height}$$

if T_2 is smaller than about 0.5 s

The second modification has been included to overcome inaccuracies in B_1.

At the beginning of the spin-echo experiment, a 90° pulse is applied, which tips the magnetisation into the y- direction. Some nuclei in the sample will precess more slowly, and others slightly faster, than the rotating frame, due to inhomogeneity in the applied field. After a time, τ a 180° pulse is applied, which inverts all the spins. At a time, 2τ the spins are rephased to give an 'echo'. At times greater than 2τ dephasing occurs. This process is represented diagramatically in Fig. 2.1b

If T_2 processes did not occur, the amplitude of the echo signal would be the same as the amplitude of the signal after a 90° pulse. T_2 processes do occur, and the decrease in the amplitude of the echo is a function of the time between the pulses, τ. A plot of echo intensity against τ will give a value for T_2.



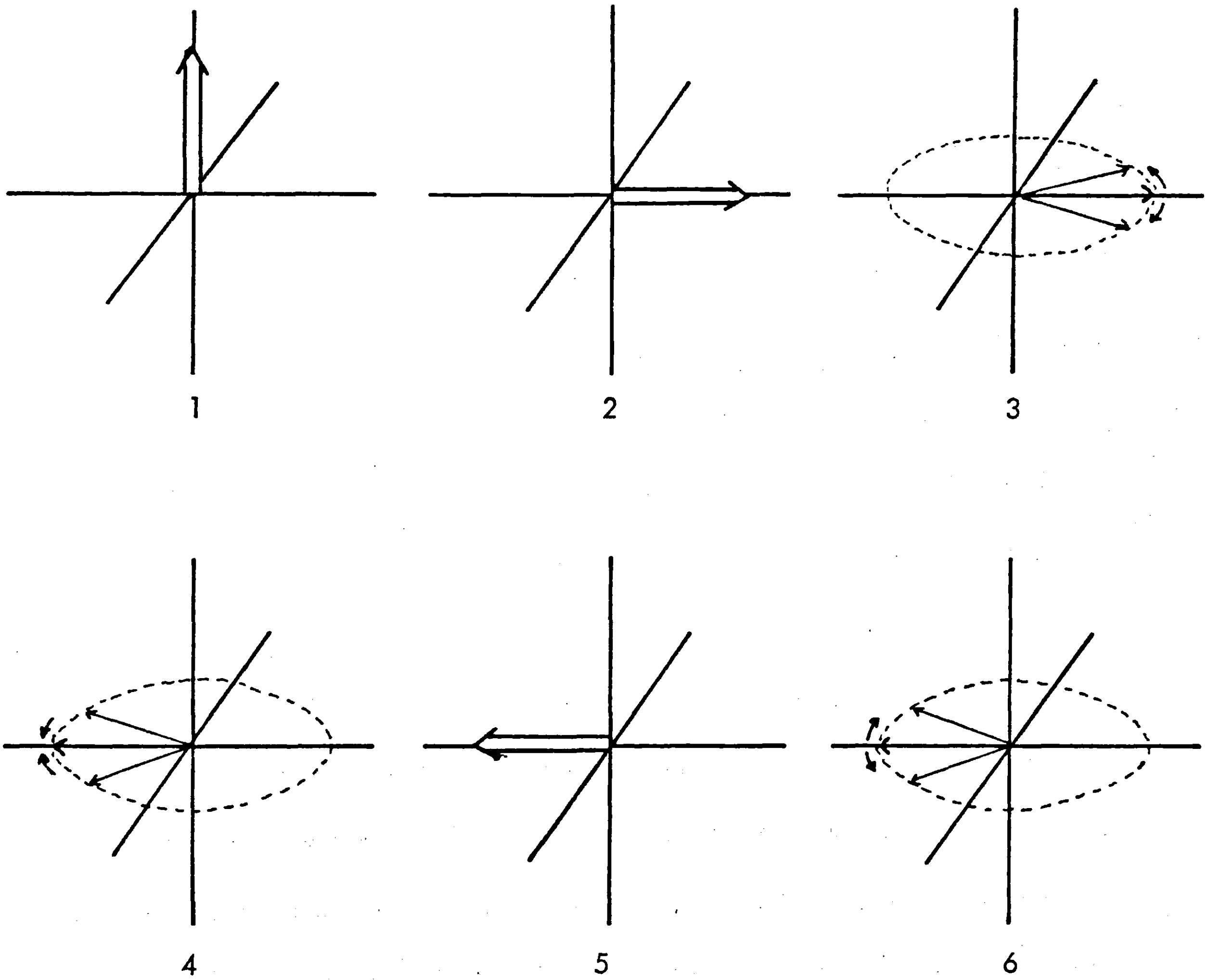


Figure 2.1(b) Diagrams showing the effect on the magnetization vector of the 90-τ-180 pulse sequence.

2.18 T_1 in the rotating frame ($T_{1\rho}$)[32]

$T_{1\rho}$ is an additional relaxation time, that may be measured by pulse F.T. methods. Normally it is measured by a spin-locking pulse sequence, which consists of a 90° pulse applied along the x-axis, followed by a long pulse of maybe seconds in length along the y-axis. The resulting FID gives a partially relaxed spectrum. The process is repeated after a wait of $5T_1$ with different values of τ . Under high resolution conditions $T_{1\rho}$ is equal to T_2.

This mechanism was not investigated for the ^{207}Pb compounds in this thesis due to the software being unavailable for the Jeol FX90Q machine. The mechanism has been briefly mentioned to show awareness of its existence.

2.19 Causes of Relaxation for nuclei with $S = \frac{1}{2}$

Relaxation times in NMR are in the order of seconds, whereas relaxation times for vibrational or rotational processes are much faster, in the order of 10^{-4} and 10^{-9} seconds respectively.

For a spin $\frac{1}{2}$, the magnetic moment depends on orientation, so any transitions between nuclear levels can only be brought about by magnetic fields.

The Boltzmann distribution law predicts information about the population of nuclear spin levels with the same temperature. Thermal relaxation to give the population at the same temperature as the bulk of the sample, only occurs via random magnetic fields in the sample. A nucleus in a liquid experiences a fluctuating field caused by the magnetic moments of nuclei in other molecules as they execute Brownian motion. The population of the spin states, change until they reach the values predicted by the Boltzmann law, for the temperature of the Brownian motion. This gives rise to the T_1 process.

The NMR linewidth is a measure of the uncertainty in the energies of the two states concerned. From the Heisenberg Uncertainty Principle, it is inversely proportional to the lifetimes of the states. The lifetimes of the states are reduced by random fluctuations of the local magnetic field. These fluctuations cause changes in the linewidths associated with T_2 and the populations associated with T_1.

2.20 A review of ^{207}Pb relaxation measurements carried out by other workers

There have been a few reports on lead-207 relaxation for various compounds. Hawk and Sharp[33,34] have studied the relaxation mechanism of lead-207 in aqueous lead perchlorate in some detail. They have found that in concentrated solutions, T_1 receives contributions from spin-rotation, dipole-dipole and chemical shift anisotropy mechanisms. The presence of the chemical shift anisotropy mechanism indicates that $PbClO_4^+$ must be present. T_2 in concentrated perchlorate solutions is shorter than expected. This is probably due to the presence of ^{17}O in the water. In more dilute perchlorate solutions, spin rotation dominates T_1 and $T_1 = T_2$.

Hawk and Sharp[35] have also studied lead-207 relaxation in liquid lead IV chloride. They have reported that T_1 decreases with increasing temperature and is dominated by the spin-rotation mechanism. T_2 is short for liquid lead IV chloride.

Relaxation time measurements have been recorded for lead telluride by Alexander and Sagalyn[36].

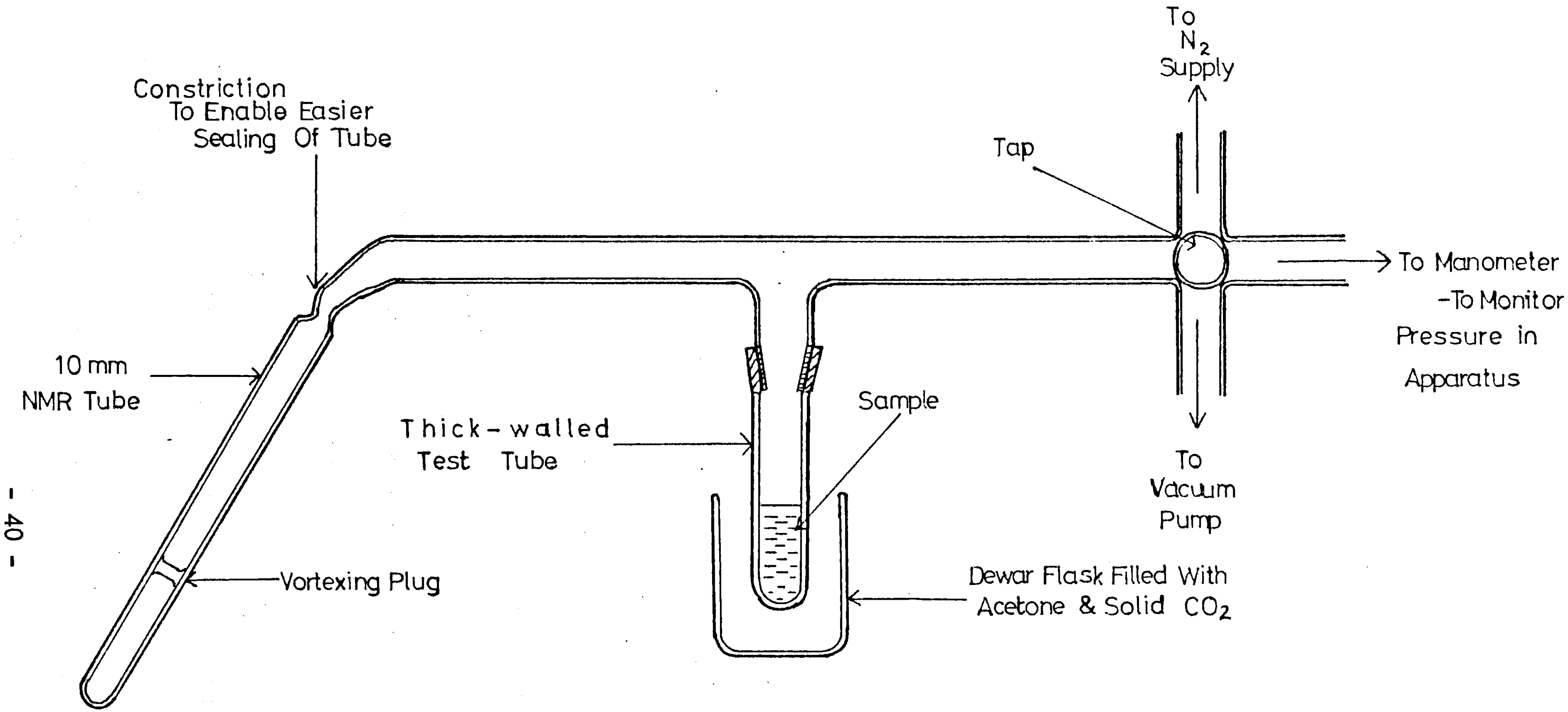
Values of T_1 for a few organolead compounds have been recorded ranging from 0.1-2s, but no mechanisms have been offered.[37]

Hays and Gillies[38] have reported T_1 values for saturated lead nitrate dissolved in D_2O, $PbMe_4$ and $PbMe_3Cl$.

2.21 Experimental

Measurements of relaxation times were obtained in the present study using four different FTNMR spectrometers: a Jeol FX90Q instrument at Bedford College, London; a Bruker WM250 at King's College, London, a Bruker WH400 at Queen Mary College, London and a Bruker WP80 at Stirling University, Scotland. All the samples were run in 10mm NMR tubes. The variable temperature studies were carried out only on the Jeol FX90Q machine because stabilising the other machines at other than room temperature was thought not to be accurate enough for the studies. All the T_1 measurements were taken using the Inversion-Recovery method. The 90° and 180° pulses used for this sequence were thought to be calibrated to an accuracy of 5-10%.[39]

It was found by experiment that longer T_1 values were obtained if the samples were thoroughly degassed before carrying out the relaxation time experiment. The solutions were therefore degassed using a series of freeze-pump-thaw cycles. Diagram 2.1 shows the apparatus used for the degassing process. The solutions could not be degassed in the NMR tube, as the tubes were too fragile to withstand large changes in temperature. The solutions were therefore degassed in a thick-walled test tube. When degassing was complete, re-dissolution was ensured and the solution was poured in a controlled atmosphere into an NMR tube which was sealed on to the apparatus. It was important to maintain a minimum level of solution



Apparatus Used For Degassing Experiment

Diagram 2.1

in the NMR tube, as too much liquid in the tube leads to inhomogeneities.[40] 'Oxygen-free' nitrogen was then introduced into the system, so that the pressure inside the NMR tube was equal to atmospheric pressure. This was carried out so that the sample could undergo variable temperature studies. Finally, the sample was sealed in the NMR tube using an oxy-acetylene flame.

Experimental T_1 measurements using undegassed samples were found to give shorter T_1 values than the same sample degassed. For example; 1 mol/dm^3 acidic lead nitrate degassed T_1 = 4.74s at 299K; 1 mol/dm^3 acidic lead nitrate undegassed T_1 = 3.00s at 299K. This indicates the importance of removing paramagnetic oxygen, which is known to provide an additional relaxation mechanism and hence to shorten the measured relaxation time. Paramagnetic oxygen may be removed and its effects modified by three methods:[41]

a) Degassing under vacuum.

b) Bubbling a diamagnetic gas through the system.

c) Chemically reducing the oxygen in the system.

Method a) has been found to be the most reliable.

T_1 measurements were carried out on a series of lead nitrate samples, a lead acetate sample and a lead tetrafluoroborate sample. Measurements were not carried out for lead perchlorate as Hawk and Sharp have investigated the system in some detail.[33,34]

Each T_1 measurement taken on the FX90Q machine was repeated on at least three separately made-up samples of the same concentration. This was to ensure that each T_1 value obtained was repeatable. These were very time-consuming experiments, so the number of different samples finally investigated was limited.

Some T_2 measurements were attempted using the Bruker WH 400, WM 250 and WP 80 machines.

2.22 Experimental Relaxation Time Measurements

2.22(a) Methods of calculating T_1 from experimental data

Two methods have been used to calculate T_1 from the experimental results. Most of the T_1 values have been calculated using the respective Jeol and Bruker NMR machine software to automatically calculate T_1. The remaining T_1 values have been calculated manually, by measuring the peak intensity and plotting a graph (see Graph 2.0) of a function of the intensity vs the τ values used, the slope of the graph being $-\frac{1}{T_1}$.

An example of T_1 calculated manually for a sample of degassed acidic lead tetrafluoroborate using the WH 400 spectrometer

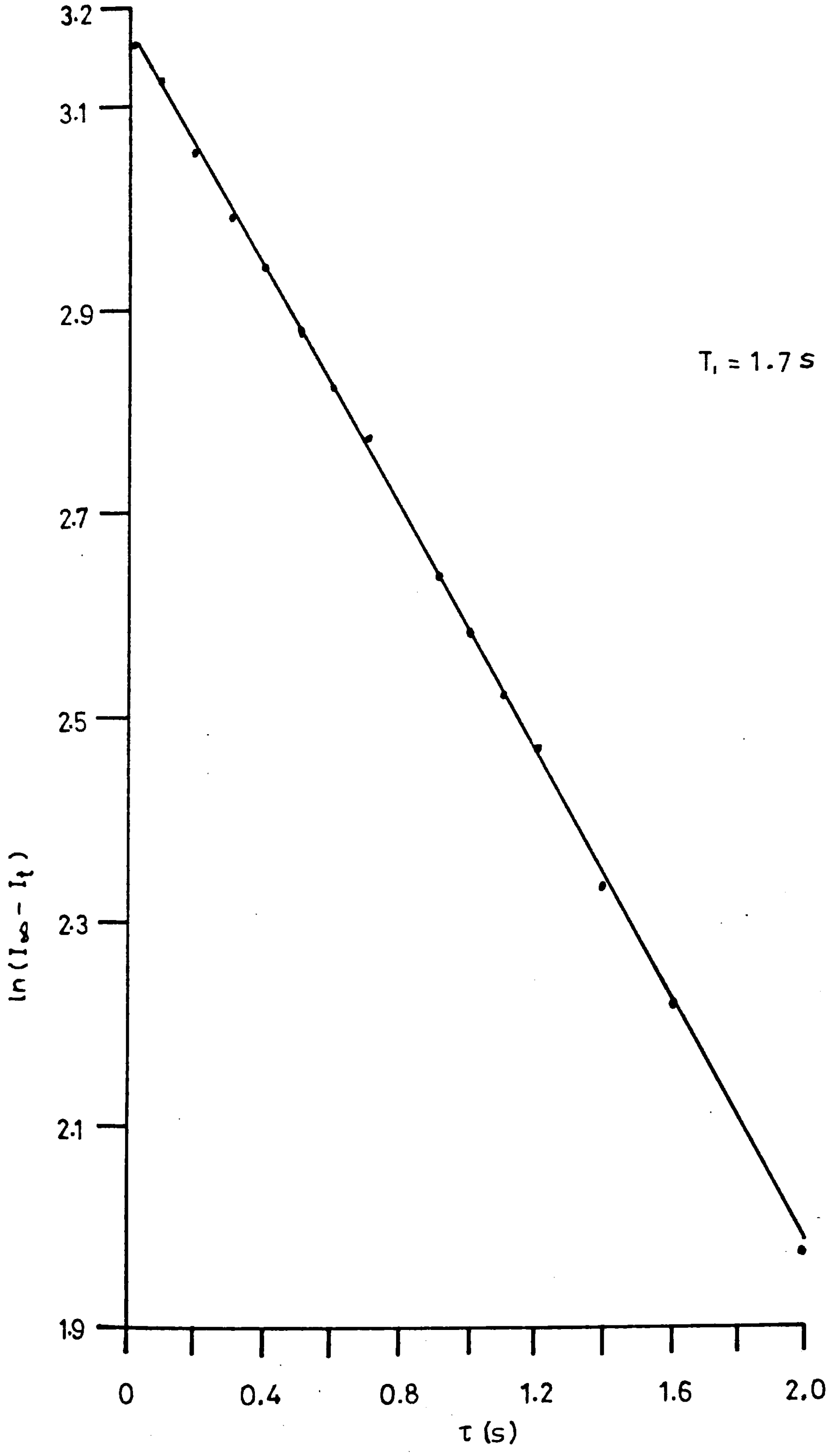
Table 2.0

I_∞ = 15.004 (using an arbitary zero), τ = 6.0 s

Intensity I_t	$(I_\infty - I_t)$	$\ln(I_\infty - I_t)$	τ (S)
22.19	7.192	1.973	2.0
24.31	9.309	2.231	1.6
25.34	10.34	2.336	1.4
26.85	11.85	2.472	1.2
27.56	12.55	2.530	1.1
28.20	13.19	2.580	1.0
29.07	14.07	2.644	0.9
30.95	15.94	2.769	0.7
31.85	16.84	2.824	0.6
32.94	17.94	2.887	0.5
34.01	19.01	2.945	0.4
34.97	19.97	2.994	0.3
36.20	21.19	3.054	0.2
37.83	22.83	3.128	0.1
38.59	23.59	3.161	0.01

PLOT FOR LEAD TETRAFLUOROBORATE ON WH 400

$\ln(I_\infty - I_t)$ AGAINST τ



GRAPH 2.0

2.22(b) Calculation of T_2[77]

The T_2 values can be calculated from peak intensity measurements obtained from the NMR experiment to measure T_2. A graph of the logarithm of the intensity vs time can be plotted. A straight line of negative slope should be obtained, with the slope being $-\frac{1}{T_2}$.

2.23 Temperature dependence studies for lead nitrate

These experiments were carried out to investigate how the spin-lattice relaxation times vary with temperature for a sample of degassed 1.00 mol/dm^3 acidic lead nitrate solution (V:V; D_2O:H_2O; 5%:95%) at 288K, 299K and 313K, on the Jeol FX90Q spectrometer. The results are shown in Table 2.1.

Table 2.1

Temperature (K)	Reciprocal Temperature K^{-1}	Spin Lattice Relaxation Time (T_1^{OBS})	$\frac{1}{T_1^{OBS}} = R_1^{OBS}$	$\ln R_1^{OBS}$
288	3.47×10^{-3}	5.30	0.19	-1.66
299	3.34×10^{-3}	4.74	0.21	-1.56
313	3.19×10^{-3}	4.42	0.23	-1.48

2.24 Concentration Dependence Studies for Lead Nitrate

This experiment was carried out to investigate the changes in spin-lattice relaxation time with concentration for a series of degassed acidic lead nitrate solutions (V:V; $D_2O:H_2O$; 5%:95%) at 299K. These experiments were carried out using the Jeol FX90Q machine. The results are shown in Table 2.2. Graph 2.2 shows a plot of T_1 changing with concentration.

Table 2.2

Concentration mol/dm^3	Spin-lattice Relaxation Time T_1 OBS (s)
1.00	4.745
0.50	4.683
0.25	3.805
0.10	3.479

One experiment was carried out using a degassed, saturated solution of lead nitrate in pure D_2O at 299K. The spin-lattice relaxation time was found to be 1.936 seconds, using the Jeol FX90Q spectrometer. Figure 2.2 shows a typical experimental T_1 plot obtained using the Jeol FX90Q spectrometer.

Spectra obtained using Jeol FX90Q spectrometer for a T_1 experiment on 0.5 mol/dm^3 acidic degassed lead nitrate solution.

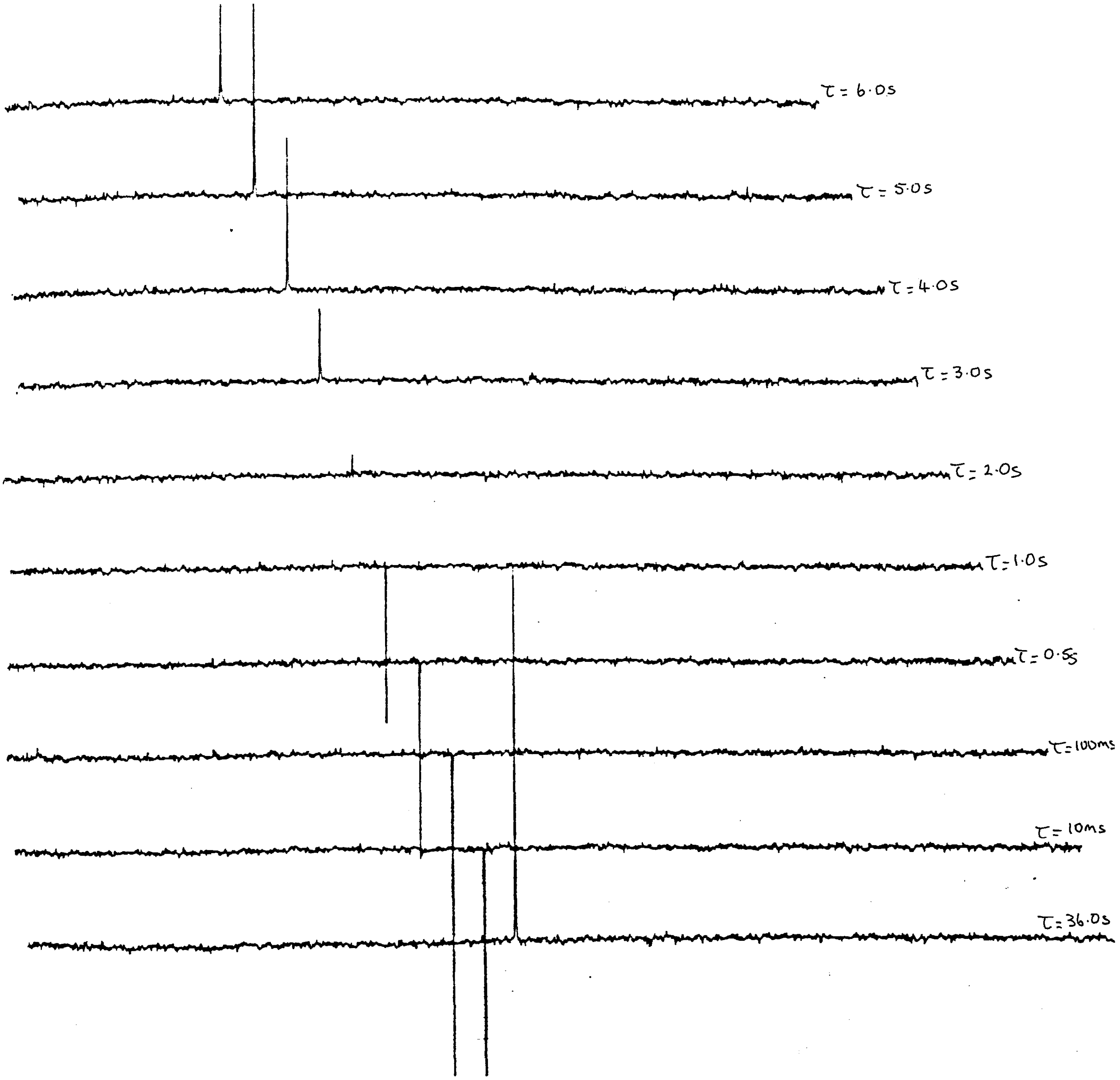
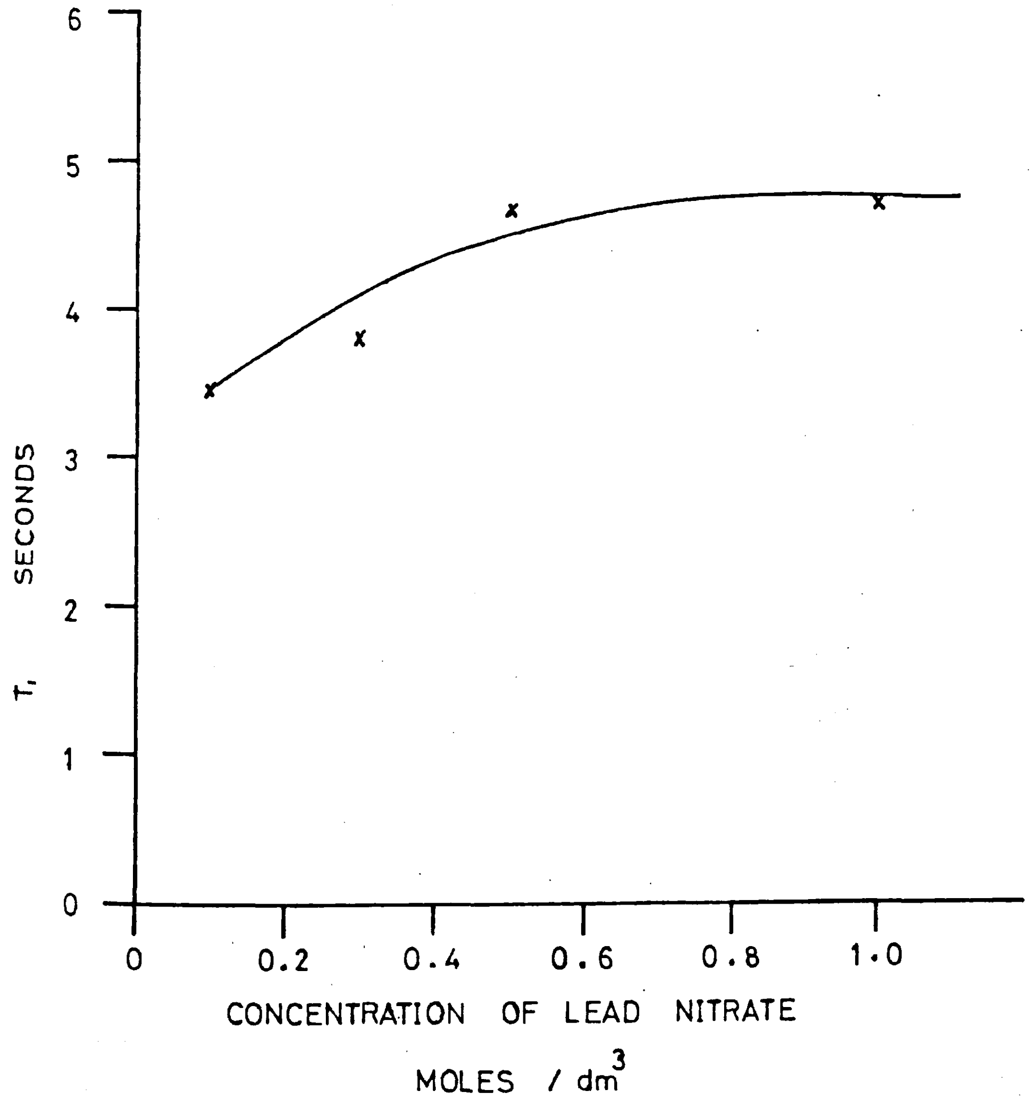


Figure 2.2

GRAPH 2.2

GRAPH SHOWING CONCENTRATION DEPENDENCE OF T_1 FOR ACIDIC SOLUTIONS OF LEAD NITRATE AT 298K



2.25 Field Dependence Studies for Lead Nitrate

This set of experiments was carried out to investigate the changes in spin-lattice relaxation time (T_1^{OBS} values) with varying the magnet strength, for a degassed sample of 1.00 mol/dm^3 acidic lead nitrate (V:V, H_2O:D_2O; 95%:5%) at 299K. These experiments led to the calculation of the percentage chemical shift anisotropy present in the T_1^{OBS} mechanism.

Table 2.3

Magnet Strength (MHz)	Field Strength (T)	T_1^{OBS} (S)	$\frac{1}{T_1^{OBS}}$ (S^{-1})	$\frac{1}{T_1^{CSA}}$ (S^{-1})	$\frac{1}{T_1^{OTHER}}$ (S^{-1})	% CSA
90	2.114	4.74	0.210	4.83×10^{-3}	0.206	2.29
250	5.870	4.17	0.239	3.95×10^{-2}	0.200	16.47
400	9.400	3.21	0.311	0.11	0.201	35.31

From the above data, T_1 values decrease with increasing field strength. This indicates that the CSA mechanism is contributing to the overall T_1 measured. If the T_1 values were equal at all field strengths, then CSA mechanism is not operating. The difference in the T_1 values at different field strengths was felt not to be due to experimental error. Graph 2.3 shows a plot of $\frac{1}{T_1}$ vs (field strength)^2. A straight line obtained from such a plot indicates the presence of the CSA mechanism.

Figure 2.3 shows the experimental plot obtained using the WM 250 spectrometer.

The percentage CSA was calculated using the following equations:

$$(T_1)^{-1}_{OBS(\omega_1)} - (T_1)^{-1}_{OBS(\omega_2)} = (T_1)^{-1}_{CSA(\omega_1)} - (T_1)^{-1}_{CSA(\omega_2)}$$

$$(T_1)^{-1}_{CSA(\omega_1)} = [\,(T_1)^{-1}_{OBS(\omega_1)} - (T_1)^{-1}_{OBS(\omega_2)}\,]\,[\,1 - \left(\frac{\omega_2}{\omega_1}\right)^2\,]^{-1}$$

The shielding tensor, σ , may be calculated from these values.[33]

If:

$$(R_1)^{CSA} = \frac{2}{15}\,\gamma^2 B_o^2 (\Delta\sigma)^2 \tau_\perp$$

Assuming $\tau_\perp$ (correlation time) $\equiv 10^{-11}$ S

γ (gyromagnetic ratio of a particular nucleus) $= 5.596 \times 10^7$ Rad T^{-1} S^{-1}

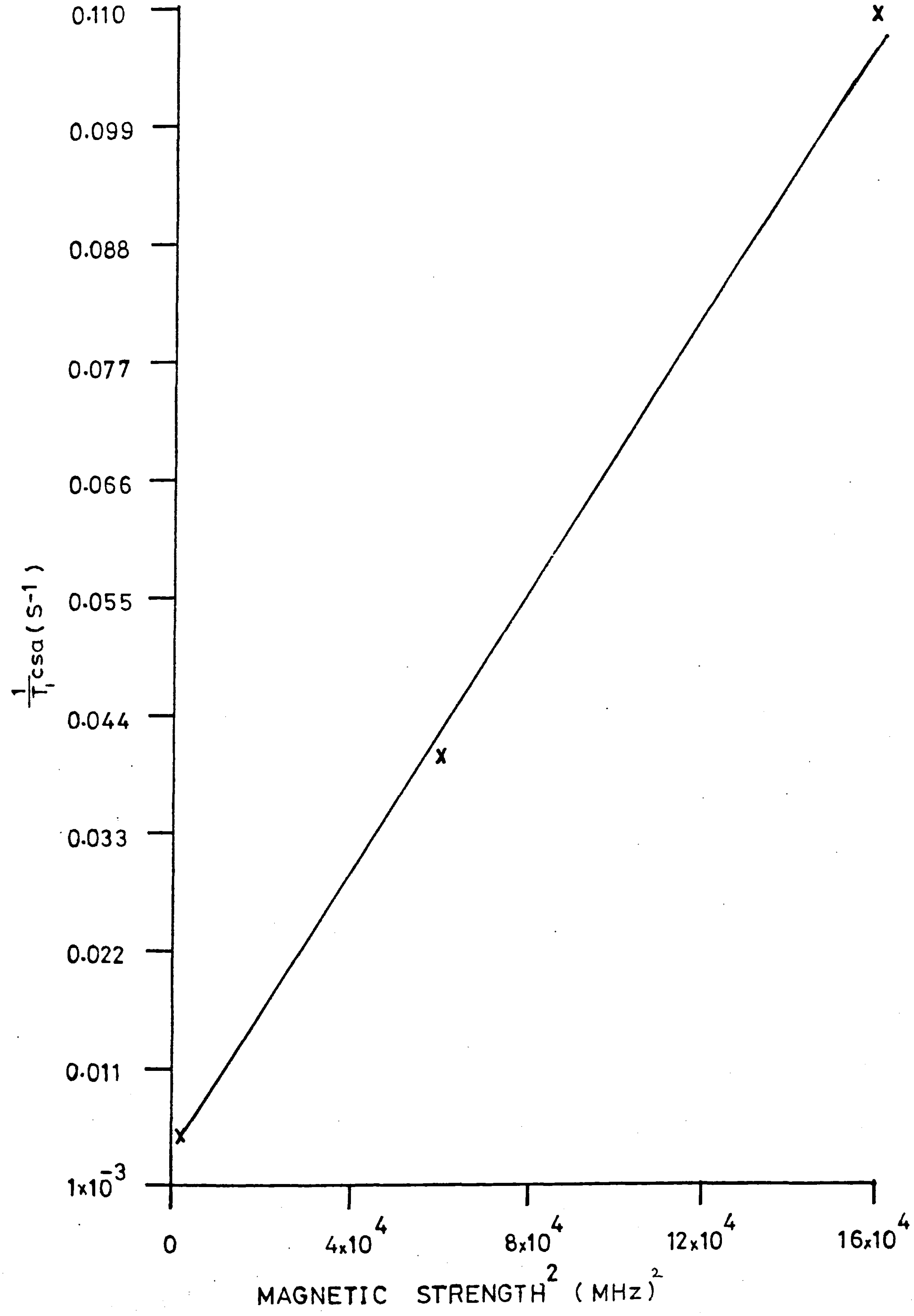
Bo (field strength) = 2.114 TESLA

$$(\Delta\sigma)^2 = \frac{4{\cdot}83 \times 10^{-3} \times 15}{2(5.596 \times 10^7)^2\,(2.114)^2 \times 10^{-11}}$$

$$\Delta\sigma \doteqdot 509 \text{ ppm}$$

The value obtained for $\Delta\sigma$ is an approximate value and very much depends upon the assumptions made in the calculation.

ACIDIC LEAD NITRATE
PLOT OF $\frac{1}{T_1}$ AGAINST MAGNETIC STRENGTH ^{2}



GRAPH 2.3

Plot of acidic degassed 0.5 mol/dm^3 lead nitrate at 296K using Bruker WM250 spectrometer.

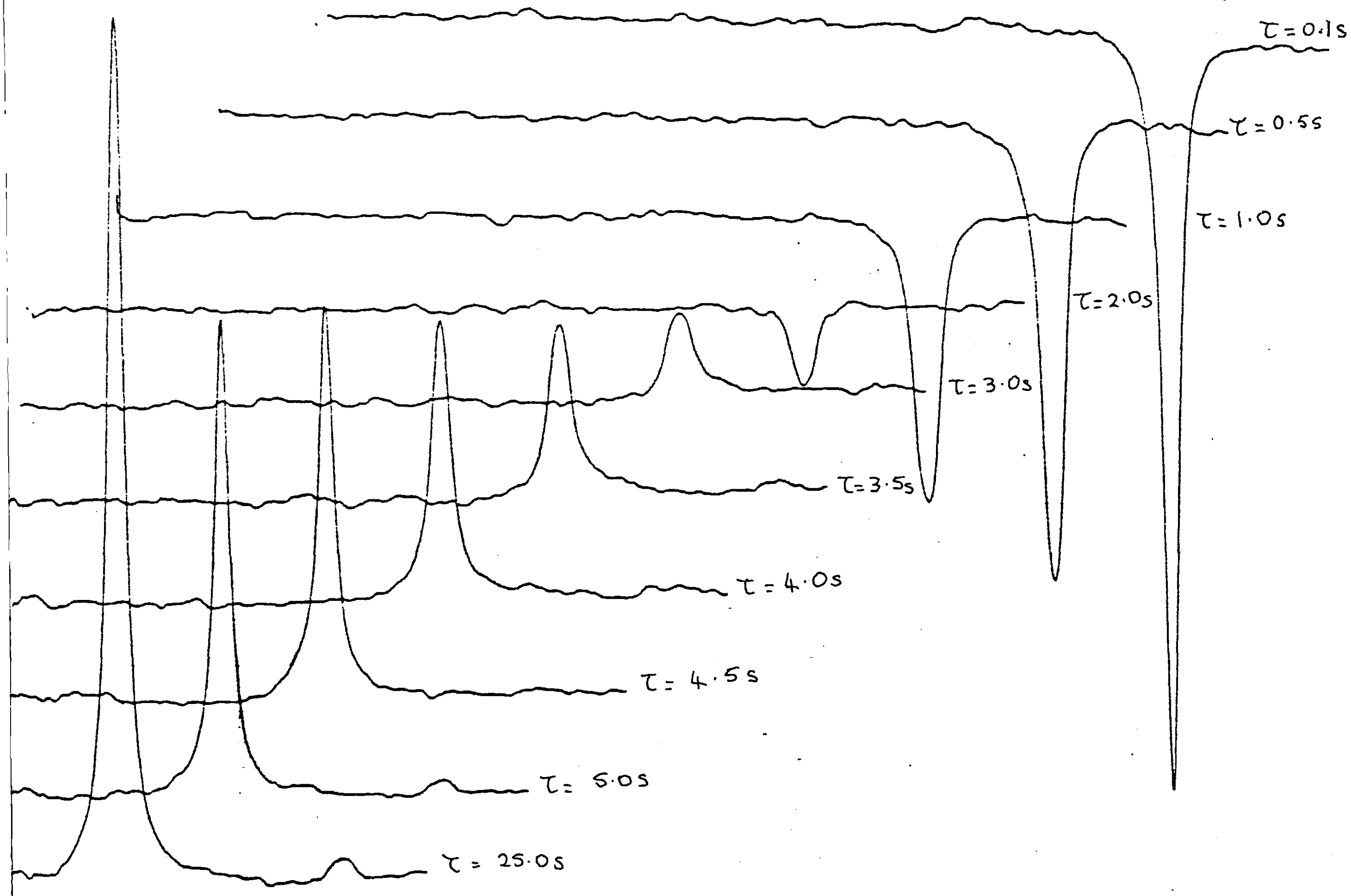


Figure 2.3

2.26 Field Dependence Studies for a Sample of Lead Tetrafluoroborate

The following experiments were carried out to investigate the changes in spin-lattice relaxation time (T_1^{OBS}) with varying the magnetic field for a degassed sample of 0.300 mol/dm^3 acidic lead tetrafluoroborate solution (V:V; D_2O:H_2O; 5%:95%) at 299K. The results are shown in Table 2.4.

Table 2.4

(MHz)	Field Strength (T)	T_1 (S)	$\frac{1}{T_1^{OBS}}$	$\frac{1}{T_1^{CSA}}$	$\frac{1}{T_1^{OTHER}}$	% CSA
90	2.114	2.29	0.436	5.80×10^{-3}	0.430	1.346
250	5.87	2.19	0.456	5.6943×10^{-2}	0.399	12·3
400	9.40	1.67	0.598	0.2019	0.396	33·7

T_1^{OBS} appeared to decrease with increasing field strength.

Figure 2.4 shows an experimental plot for the above experiment on the Jeol FX90Q spectrometer.

Experimental plot of acidic degassed lead tetrafluoroborate at 296K using Jeol FX90Q spectrometer

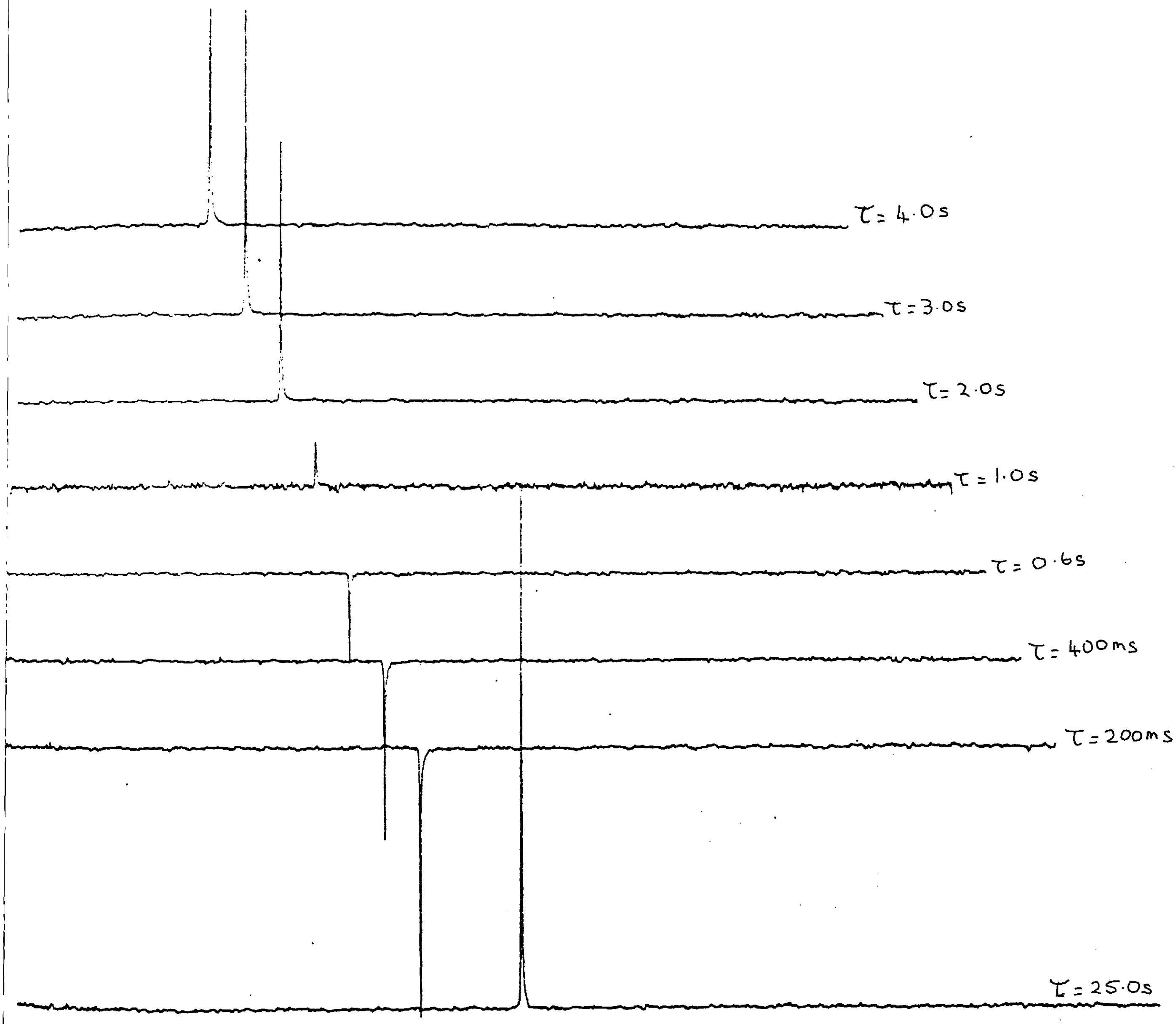


Figure 2.4

2.27 Field Dependent Studies for Lead Acetate

These experiments were carried out to investigate the changes in the spin-lattice relaxation time (T_1^{OBS}) with varying magnetic field for a degassed sample of 0.500 mol/dm^3 acid lead acetate solution (V:V; D_2O:H_2O; 5%:95%) at 299K.

The spectrometers used for this study were the Bruker WP 80 at Stirling University, the Bruker WM 250 at King's College, London, the Bruker WH 400 at Queen Mary College, London and the Jeol FX90Q at Bedford College, London.

The experimental results are shown in Table 2.5.

Table 2.5

Magnet Strength (MHz)	T_1^{OBS} (S)
80	0.293
90	0.356
250	0.146
400	0.108

Figures 2.5 and 2.6 show the experimental results obtained on the WH 400 and WP 80 machines for the above experiments.

Experimental plot for acidic degassed lead acetate at 296K using a Bruker WH400 spectrometer.

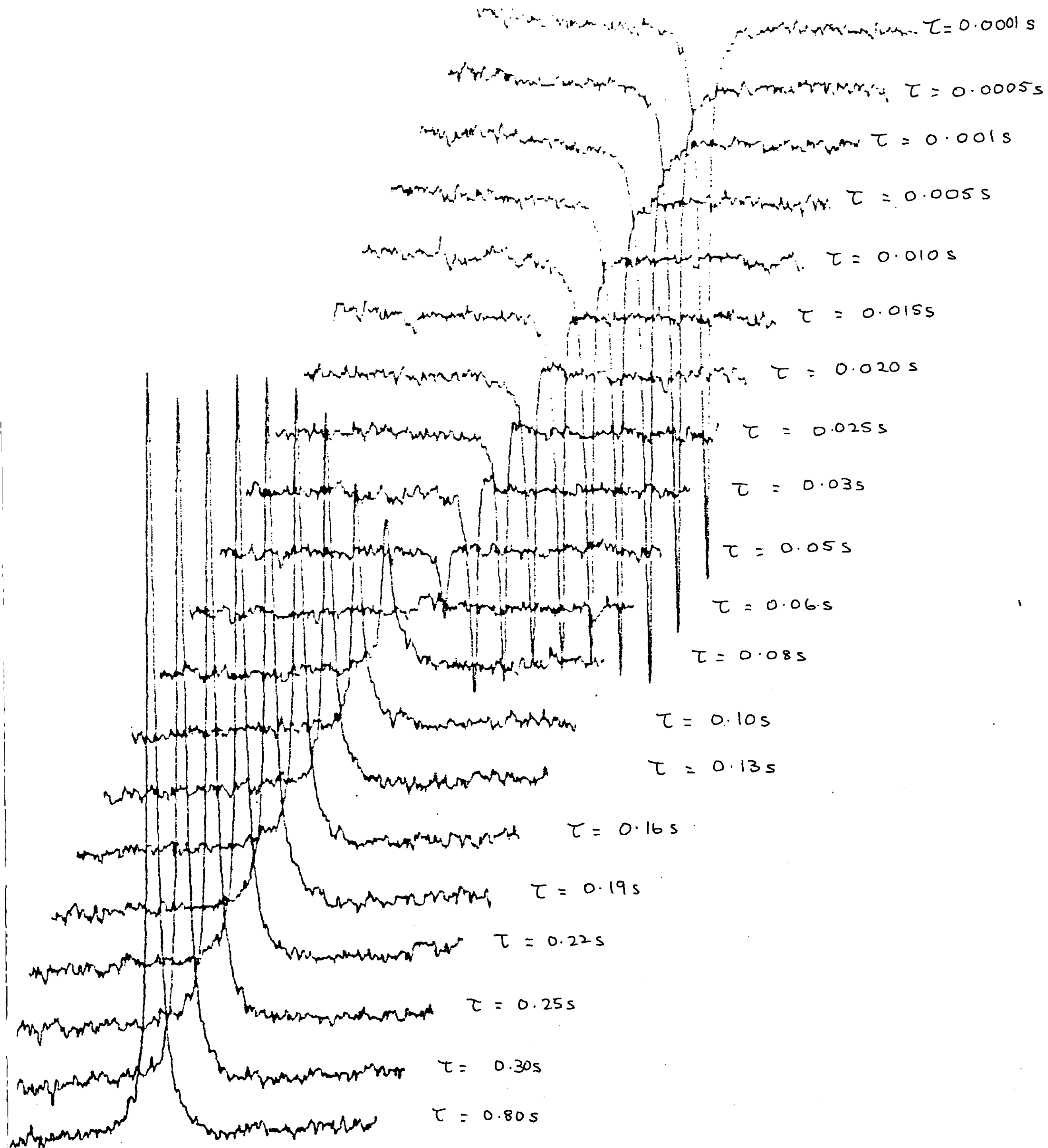
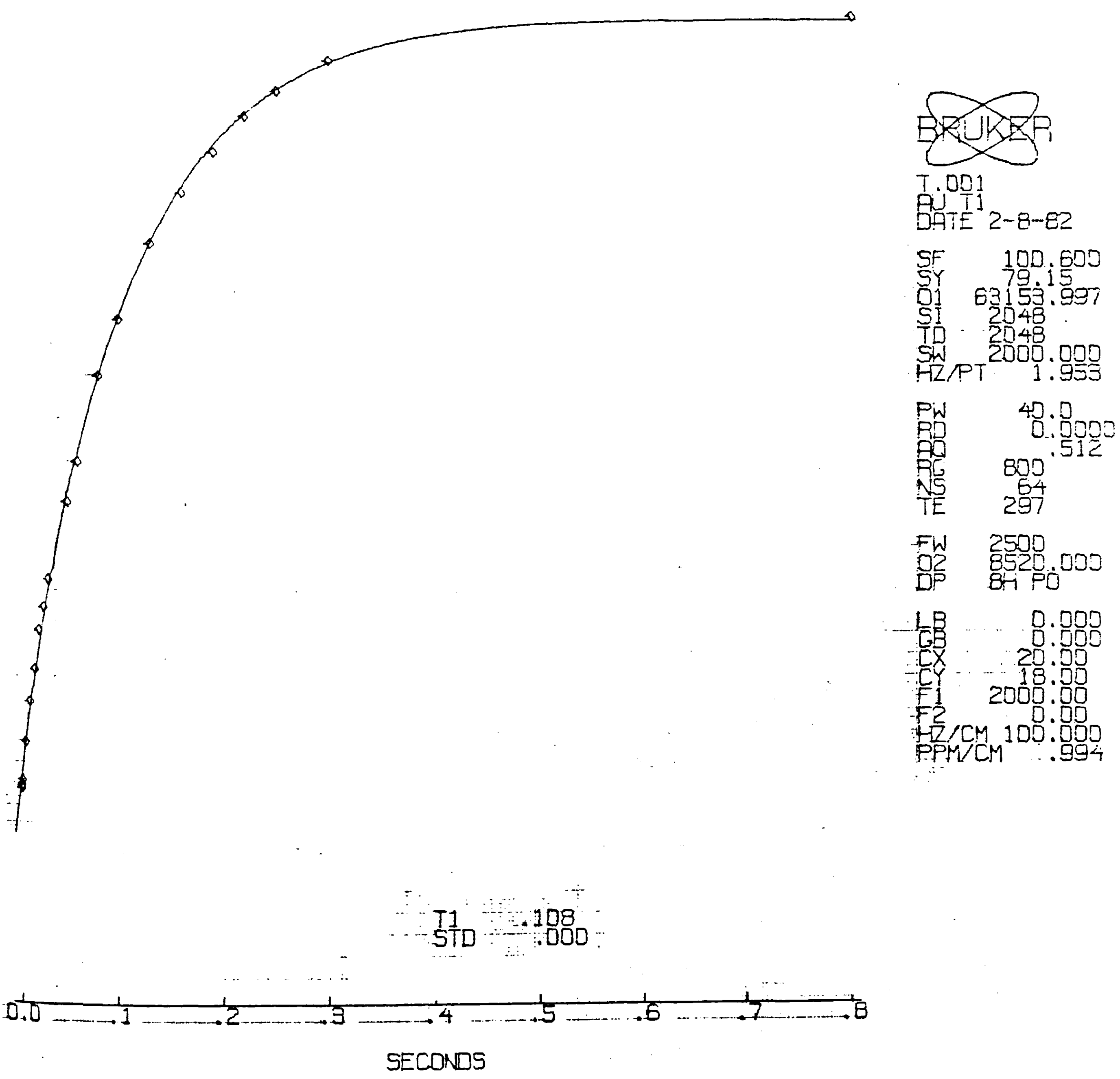


Figure 2.5(a)

Print out of calculation of T_1 for spectra shown in Figure 2.5(a)



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TE      297

FW     2500
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GB        0.000
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CY       18.00
F1     2000.00
F2        0.00
HZ/CM  100.000
PPM/CM    .994
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STD    .000
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Figure 2.5(b)

Spectra for T_1 for acidic degassed 0.5 mol/dm^3 lead acetate using a Bruker WP80 spectrometer at 296K

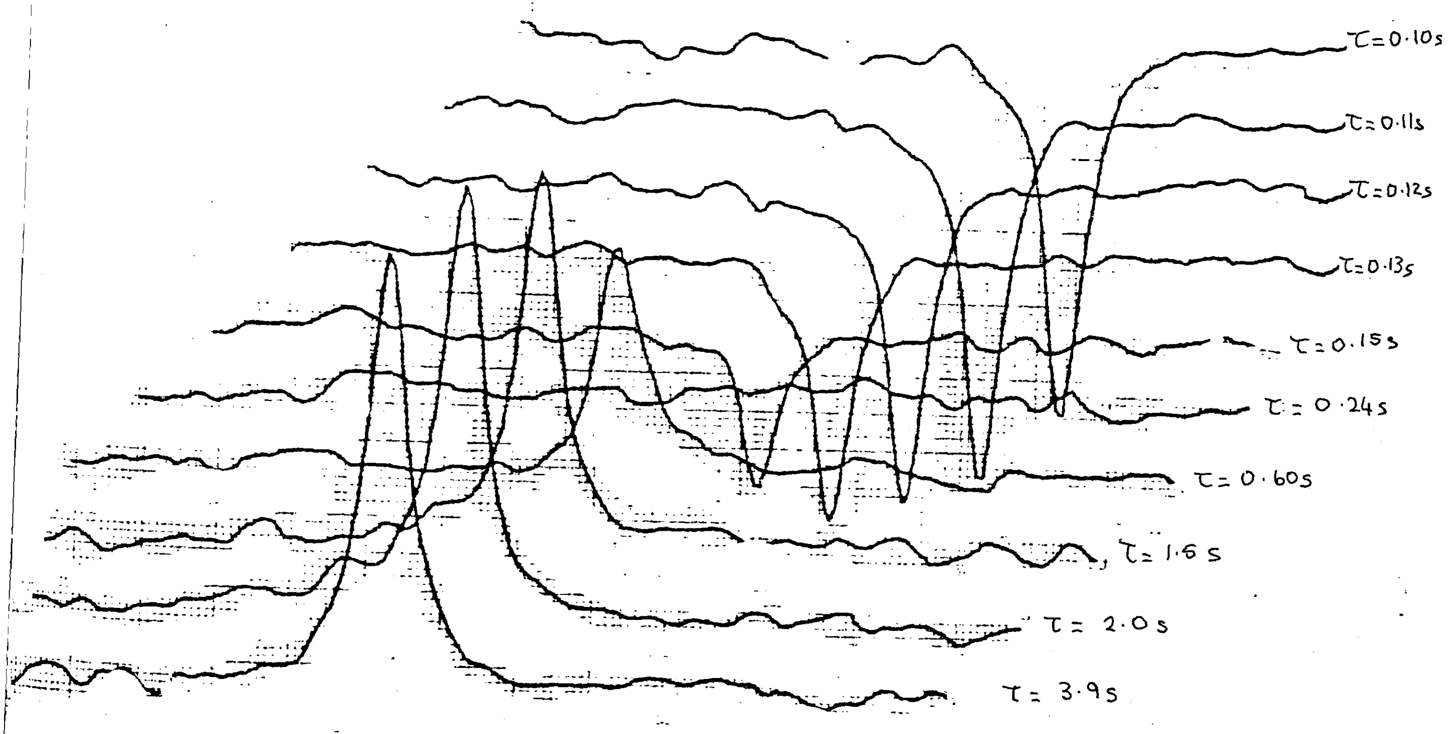
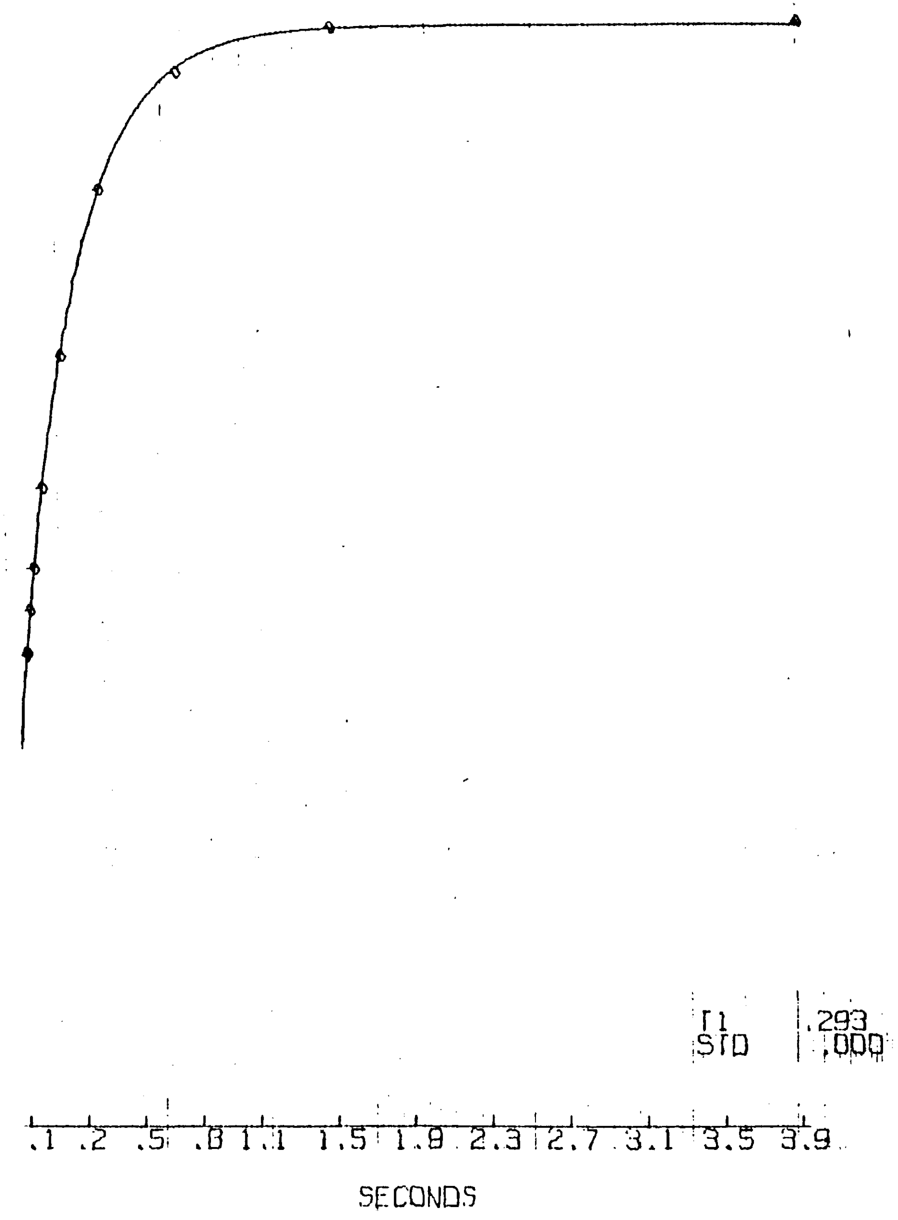


Figure 2.6(a)

Figure 2.6(b) Plot of results from 2.6(a)



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TE      305

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CY       12.00
F1      863.28
F2      394.53
HZ/CM    31.250
PPM/CM    1.867
SA     2000.00
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2.28 T_2 Measurements

T_2 measurements were carried out using three different Bruker NMR machines, WH 400, WM 250 and WP 80. T_2 results were not obtained using the Jeol FX90Q machine due to the unavailability of the software to run such an experiment.

The following results given in Table 2.6 were obtained using the Hahn method[29]. The Bruker program used to obtain the experimental data can be found in the appendix.

Table 2.6

Temperature (K)	NMR machine used	Compound	T_2 value (S)
296	WH 400	Acidic degassed lead nitrate 0.5 mol/dm^3	0.453
296	WM 250	Acidic degassed lead nitrate 0.5 mol/dm^3	6.57
296	WP 80	Acidic degassed lead acetate 0.5 mol/dm^3	0.092

Figure 2.7 shows the experimental plot obtained for the T_2 run for the lead acetate sample on the WP 80 machine.

The accuracy of the experimental T_2 values is uncertain, so there are discrepancies between the quoted values.

Spectra for T_2 experiment for acidic degassed 0.5 mol/dm^3 lead acetate sample using a Bruker WP80 machine.

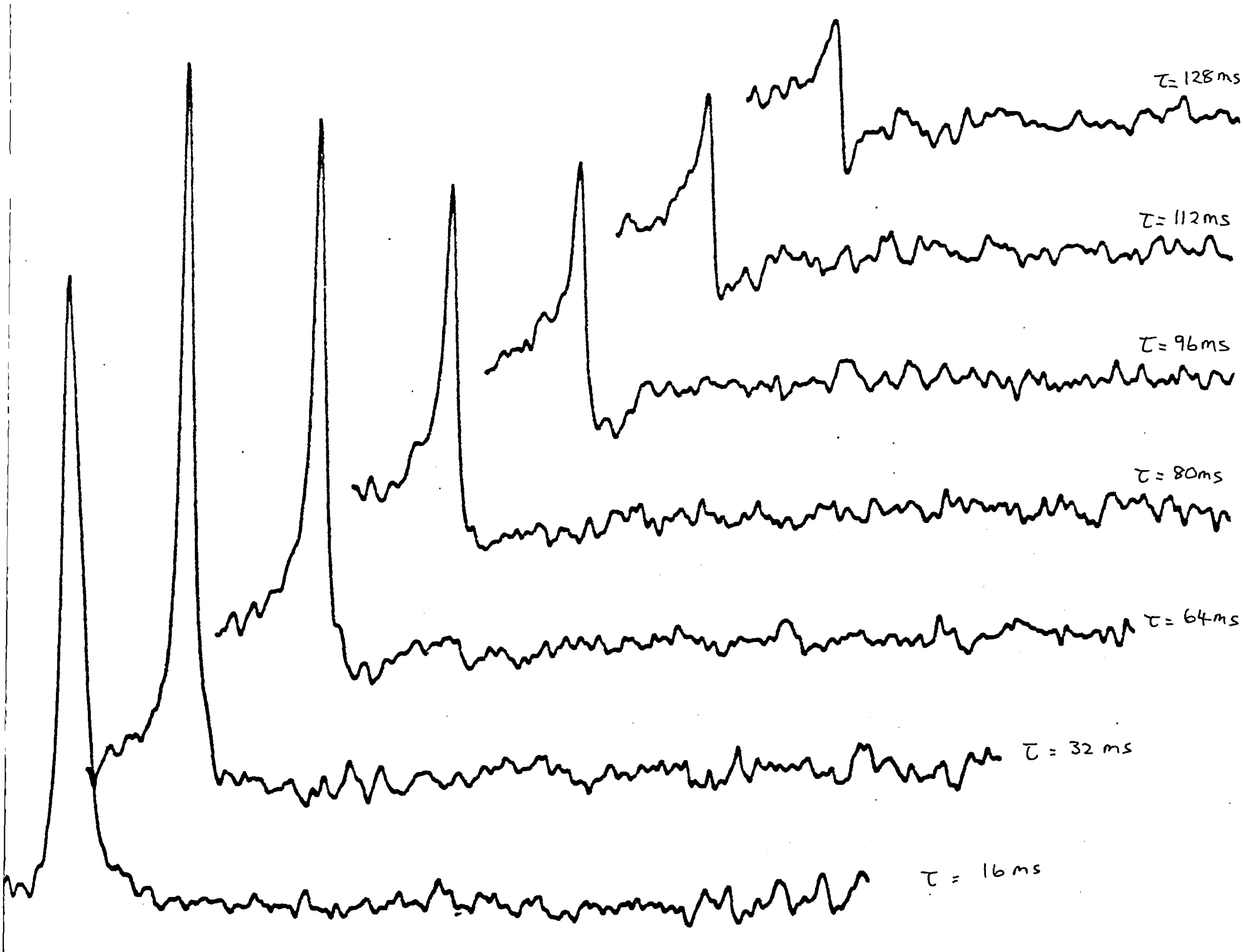


Figure 2.7

2.29 Conclusion

Generally relaxation times refer to changes of translational and reorientational correlation times with varying temperature and concentration. When the spin quantum number, I , is $\frac{1}{2}$, the chemical shift anisotropy mechanism may contribute strongly to the overall $T_1^{OBSERVED}$ value. In all cases the T_1^{OBS} value is thought to have been obtained with an accuracy of 5-10%.[39]

The relaxation times of the ^{207}Pb nucleus in the compounds studied, probably result from a variety of interactions. Information relating to the hydration sphere around the ^{207}Pb nucleus could be obtained if the interactions could be separated. The hydration properties of the Sr^{2+} nucleus have been investigated and it has been suggested that the Pb^{2+} nucleus would have similar properties to the Sr^{2+} nucleus, due to the nuclei having similar heats of hydration and also similar ionic radii.[33]

The value of the observed T_1 value for lead nitrate has been found to decrease with increasing temperature. This indicates a contributory mechanism leading to the T_1^{OBS} value, which is temperature dependent. The Arrhenius plot obtained for these results indicates the presence of a spin rotation mechanism. The activation parameters obtained from an Arrhenius plot should be analysed with caution, as the values are not obtained with very high precision.[42]

The results obtained for t he field dependence studies for lead nitrate and lead tetrafluoroborate show a decrease in T_1^{OBS} with increasing field strength. The contribution due to the CSA mechanism has been calculated, and the presence of this mechanism indicates that the Pb^{2+} nucleus is not entirely in an isotropic environment.

The lead acetate field dependence results do show a large difference between the T_1 values at different field strengths. T_1 due to the CSA mechanism is thought to play an important role in this case.

Generally, scalar coupling is not thought to be a contributory mechanism responsible for T_1^{OBS} in lead compounds. The ^{207}Pb nucleus is a spin ½ nucleus, so the quadrupolar mechanism is not relevant in this case. The NOE has been found to be zero in the cases considered here, although the maximum NOE for this nucleus in some compounds[42] has been found to be + 3.41. Zero NOE means that the dipolar mechanism is not important. From these deductions, the T_1^{OBS} mechanism in the ^{207}Pb compounds studied was probably due to a combination of the spin rotation mechanism and the chemical shift anisotropy mechanism. The $(T_1^{OTHER})^{-1}$ results shown in tables 2.3 and 2.4 are quite consistent with the deductions. This supports the idea that only one other mechanism is involved in the relaxation, to any great extent.

It has been suggested[43] that if the 90° pulse is found to be longer than 30-40, μs, then the T_1 experiment would not be successful. The 90° pulse for the lead compounds studied was found to be shorter than 30 μs.

The T_2^{OBS} values obtained were found to be different from the corresponding T_1^{OBS} values for each sample. The results shown in table 2.6 were not expected, as T_1^{OBS} was expected to be equal to T_2^{OBS}, the difference in the values could be due to exchange mechanisms affecting the results. T_2^{OBS} values have been found to be less than the corresponding T_1^{OBS} values for some other nuclei, for example, Silver and Yttrium isotopes.

CHAPTER THREE

LEAD-207 NMR
CHEMICAL SHIFT

A Review of ^{207}Pb NMR Studies carried out by other Workers

3.1a Chemical Shift

Early studies of ^{207}Pb NMR were carried out using broad line techniques.[44,45] These studies consisted of measurements made using both liquid and solid samples; and demonstrated that there was a ^{207}Pb chemical shift range of around 8000 ppm (excluding lead metal measurements). Similar studies indicated that tetramethyl lead was to be found in about the middle of the reported chemical shift range.[46] Tetramethyl lead has been used as a reference for some ^{207}Pb NMR data, while 1 mol/dm^3 lead nitrate, 0.1 mol/dm^3 lead perchlorate or a lead perchlorate value at infinite dilution, have been used as a reference in other papers.

A comparatively small amount of NMR work has been carried out using the ^{207}Pb nucleus, although Maciel and Dallas[47] in 1973 suggested that FTNMR could be a very good method for studying the chemistry of lead. About half the work published until 1979, on the lead nucleus, was carried out using double resonance techniques.[48,49,50] Fourier transform methods have recently become more important for studying the ^{207}Pb nucleus.

Minor structural variations in the lead environment seem to give rise to large shifts. This implies that ^{207}Pb chemical shift measurements may be very useful for dynamic and structural studies of lead compounds. The measurements may also be useful in analytical applications.

The effects of solvent and concentration on ^{207}Pb shifts have been somewhat neglected.[51] It has been suggested that these effects are quite unimportant, unless there is a direct chemical interaction between the lead nucleus and its changing environment. However a shift of 31 ppm has been reported on going from a 1 mol/dm^3 lead nitrate solution in water to a 1 mol/dm^3 lead nitrate solution in deuterium oxide.

Spectra for four coordinate lead species have been reported[52,53] and some work has been carried out comparing lead and tin NMR data. Lead is more sensitive to changes in substituents than tin, which is reasonable in view of the greater polarisability of lead. Generally, factors controlling shielding appear to be similar for both tin and lead.[47,49,54]

^{207}Pb shielding appears to be dominated by the paramagnetic term.[46] By increasing the electron withdrawing ability of the substituents, the lead shielding decreases. Shielding can be increased by the presence of bulky substituents. The shielding of the ^{207}Pb nucleus has been investigated in several publications. Lutz and Nolle[55] have examined the shielding tensors for lead, in aqueous lead nitrate. Lutz and Stricker[56] have investigated the magnetic moment and shielding of lead ions in water, while Nolle[57] has investigated ^{207}Pb magnetic shielding anisotropy in several lead compounds, for example; lead nitrate, lead chromate and lead carbonate by FTNMR.

Solid NMR spectra of lead compounds have led to important conclusions about the effect of coordination number on lead shielding.[45,58,59]

Shifts for various lead containing compounds have been reported by Kim and Bray,[60] and there have been several reports of shifts for organolead compounds.[61,62,63,64]

3.1b Coupling Constants

Very few coupling constants have been measured between lead and nuclei other than protons. For one bond coupling, the lack of data is probably due to the instability or preparation difficulty of suitable species.

Double resonance data are useful for investigating coupling constants, as they facilitate fast working and identification of species in mixtures by showing the relationship between the resonances of the protons and the lead nuclei.

Lead-lead coupling has been reported for hexamethyldilead.[65,66] Close parallels between coupling constants for tin and lead have been found in alkyl compounds, but such parallels have not been found for aryl compounds.[67] Normally the lead coupling constants are larger by 20-50% than in the analogous tin compounds, and are of opposite sign, due to the magnetogyric ratio of lead being positive, while the magnetogyric ratio of tin is negative.[68]

Two or three bond couplings between carbon and lead have been briefly examined. It has been found that when the coupling path involves atoms other than sp^3 carbon, interesting variations in sign and magnitude arise, especially when small s-overlap integrals occur in bonds involved in coupling paths.[69,70]

Few studies of lead coupled over more than three bonds have been carried out, but these data have shown that the relevant ^{207}Pb satellites are generally more easy to see than the corresponding satellites from tin.[71-74]

Indirect nuclear spin-spin interactions in lead have been determined using spin-echo techniques.[75]

Coupling constants to other magnetic nuclei, for example, boron, phosphorus, nitrogen, tin and selenium have also been briefly examined.[48]

3.2 Experimental

Chemical shift measurements were obtained using a Jeol FX90Q Fourier Transform Nuclear Magnetic Resonance Spectrometer at Bedford College. The samples were run using 10 mm NMR tubes, in a tunable multinuclear probe. The temperature of the samples was controlled by a JEOL NM-VTS control unit, with the operating accuracy, reported by the manufacturers, to be $\pm 0.5^{\circ}C$ in the vicinity of the sample.

The majority of the solutions were obtained using commercially obtained chemicals, but some of the compounds investigated were synthesised.

Solutions of the same compound at different concentrations were made up from stock solutions whenever this method was possible, as inaccuracies do occur when compounds are weighed out each time. As it was impossible to weigh out an accurate sample of lead perchlorate, due to the hydroscopic nature of the salt, the solution was made up and then analysed to find the lead content by determining the lead content gravimetrically as the chromate salt.[76]

Deuterated water was added internally to each sample (5% by volume) as the locking material in all the aqueous solutions. This was thought to be the lowest concentration required to maintain a constant lock of reasonable signal intensity. Higher concentrations of Deuterium Oxide have been found to affect the position of the resonance signal of the nucleus under investigation. For the acidic solutions, an appropriate acid (often containing the same anion as the lead compound) was added to each solution.

Using distilled or deionised water did not seem to affect the position of the ^{207}Pb resonance signal.

All the chemical shift data reported for ^{207}Pb nucleus, in ppm, have been referenced from a value of lead perchlorate at infinite dilution at that temperature. This value was obtained by short extrapolation.

3.3 The sample in the NMR tube

The tubes were made of Pyrex and were cylindrical in shape with walls of uniform thickness. The tubes were cleaned after each experiment with soapy water followed by rinsing in tap water, then washed with dilute hydrochloric acid and then washed several times with distilled water and allowed to dry on clean tissue. Any organic material in the tubes was removed with acetone or concentrated acid before washing the tube in soapy water.

It was very important to take care when filling the tube because a convenient height of liquid above the receiving coil is needed. Incorrect sample height may affect the resolution, sensitivity and the accuracy of measurements, especially relaxation time measurements.

Occasionally several ^{207}Pb peaks were observed in one sample, a spectral width away from each other. Any real peak was found by testing each peak to see if it behaved in a predicted way. The peak was considered to be real if,

1) The signal occurred at all sweep widths and gave a consistent value for its resonance frequency.
2) The signal moved in a predicted manner with changing the value of the OFFSET parameter on any sweep width.
3) The signal gave a sinusoidal FID.
4) The transformed signal phased correctly.

3.4 Results for ^{207}Pb Chemical Shift Measurements

Table 3.1: Chemical Shift Data for Acidic Solutions of Lead Perchlorate

The following table shows the effect of changing the concentration and temperature for a series of acidic lead perchlorate solutions (V:V $D_2O:H_2O$ 5%:95%) at pH 1.26

Temperature (K)	Concentration Lead Perchlorate (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
278	1.600	18693.000	74.3
278	1.370	18692.860	66.8
278	0.920	18692.550	50.2
278	0.460	18692.159	29.3
278	0.230	18691.870	13.9
278	0.090	18691.709	5.2
278	0.020	18691.634	1.3
278	0.0040	18691.620	0.5
278	Infinite Dilution	18691.610	0.0
288	1.600	18693.040	72.7
288	1.370	18692.900	65.2
288	0.920	18692.595	48.9
288	0.460	18692.205	28.0
288	0.360	18692.110	23.0
288	0.230	18691.960	14.9
288	0.090	18691.810	6.9
288	0.450	18691.750	3.7
288	0.0230	18691.730	2.6
288	0.0090	18691.690	0.5
288	Infinite Dilution	18691.680	0.0

Table 3.1 (continued)

Temperature (K)	Concentration Lead Perchlorate (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
299	2.000	18693.450	94.2
299	1.600	18693.005	70.3
299	1.370	18692.882	63.6
299	0.920	18692.595	48.4
299	0.460	18692.265	30.7
299	0.360	18692.210	27.8
299	0.230	18692.065	20.0
299	0.090	18691.895	10.9
299	0.0450	18691.835	7.7
299	0.0230	18691.805	6.1
299	0.0090	18691.770	4.2
299	0.0050	18691.700	0.5
299	Infinite Dilution	18691.690	0.0
313	1.600	18693.035	56.4
313	1.300	18692.935	51.0
313	0.920	18692.690	37.9
313	0.460	18692.410	23.0
313	0.230	18692.225	13.1
313	0.090	18692.090	5.8
313	0.040	18692.040	3.2
313	0.020	18692.010	1.6
313	0.009	18691.990	0.5
313	Infinite Dilution	18691.980	0.0

Table 3.1 (continued)

Temperature (K)	Concentration Lead Perchlorate (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
333	1.600	18693.110	46.5
333	1.300	18693.020	41.7
333	0.920	18692.815	30.7
333	0.460	18692.565	17.3
333	0.360	18692.520	14.9
333	0.230	18692.405	8.8
333	0.090	18692.310	3.7
333	0.040	18692.270	1.6
333	0.020	18692.260	1.0
333	0.0090	18692.250	0.5
333	Infinite Dilution	18692.240	0.0
353	1.600	18693.210	42.2
353	1.300	18693.010	31.5
353	0.920	18692.930	27.2
353	0.460	18692.700	14.9
353	0.360	18692.640	11.7
353	0.230	18692.560	7.4
353	0.090	18692.470	2.6
353	0.040	18692.460	2.1
353	0.020	18692.440	1.0
353	Infinite Dilution	18692.420	0.0

GRAPH 3.1

GRAPH OF RESONANCE FREQUENCY CHANGING WITH CONCENTRATION AND TEMPERATURE FOR A SERIES OF ACIDIC LEAD PERCHLORATE SOLUTIONS

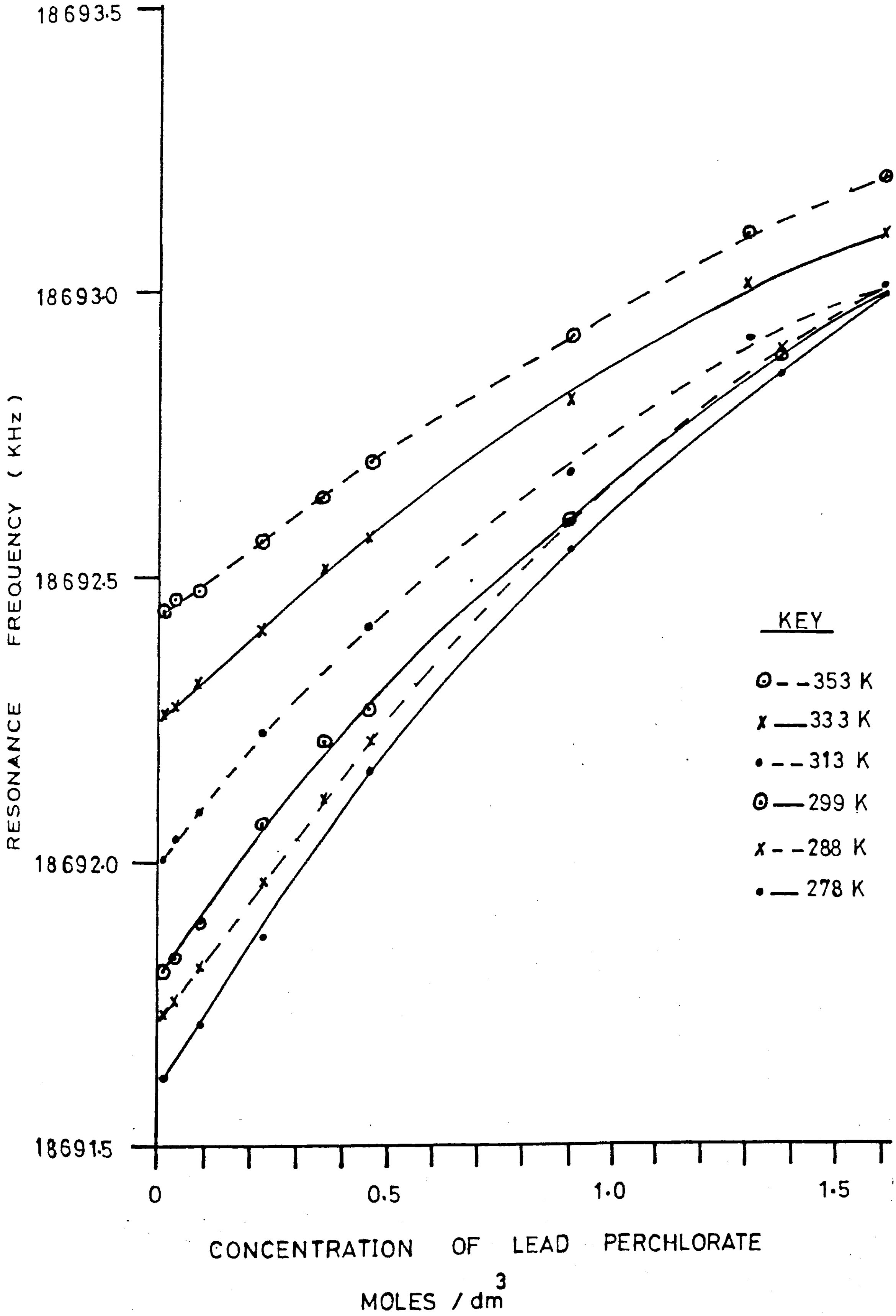


Table 3.2 The effect of pH on ^{207}Pb signal in Lead Perchlorate Solution

This set of experiments was carried out to examine the effect of changing the pH of a 0.25 mol/dm^3 solution of lead perchlorate at 299K.

pH	Volume of 0.3 mol/dm^3 Lead Perchlorate (mls)	Volume of 0.3 mol/dm^3 Perchloric Acid (mls)	Volume of 0.3 mol/dm^3 Sodium Hydroxide (mls)	Volume of Water (mls)	Resonance Frequency (KHz)	Chemical Shift (ppm)
1.03	25.00	5.00	0.00	0.00	18692.090	21.4
1.63	25.00	1.00	0.00	4.00	18692.100	21.9
1.94	25.00	1.00	1.00	3.00	18692.100	21.9
4.09	25.00	1.00	3.00	1.00	18692.280	31.6
4.16	25.00	1.00	4.00	0.00	18692.280	31.6

Table 3.3: Lead Tetrafluoroborate in Acidic Solution

The following table shows the chemical shift data for a series of acidic lead tetrafluoroborate solutions at various concentrations and temperatures, using D_2O and water as the solvent (V:V $D_2O:H_2O$ 5%:95%)

Temperature (K)	Concentration of Lead Tetrafluoroborate (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
288	1.050	18692.810	60.5
288	0.920	18692.720	55.6
288	0.790	18692.590	48.7
288	0.660	18692.440	40.7
288	0.530	18692.325	34.5
288	0.390	18692.195	27.6
288	0.260	18692.055	20.1
288	0.130	18691.885	10.9
288	0.070	18691.795	6.2
288	0.030	18691.720	2.1
288	0.010	18691.720	2.1
299	1.050	18692.950	67.4
299	0.920	18692.830	60.9
299	0.790	18692.720	55.1
299	0.660	18692.580	47.6
299	0.530	18692.475	41.9
299	0.390	18692.355	35.6
299	0.260	18692.240	29.4
299	0.130	18692.110	22.5
299	0.070	18692.020	17.7
299	0.030	18691.980	15.5

Table 3.3 (continued)

Temperature (K)	Concentration of Lead Tetrafluoroborate (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
313	1.050	18692.970	52.9
313	0.920	18692.820	44.9
313	0.790	18692.765	41.9
313	0.660	18692.675	37.2
313	0.530	18692.580	32.1
313	0.390	18692.420	23.5
313	0.260	18692.350	19.8
313	0.130	18692.240	13.9
313	0.070	18692.195	11.5
313	0.030	18692.040	3.2
313	0.010	18692.080	5.4

GRAPH 3.3

GRAPH OF RESONANCE FREQUENCY CHANGING WITH CONCENTRATION AND TEMPERATURE FOR A SERIES OF ACIDIC LEAD TETRAFLUOROBORATE SOLUTIONS

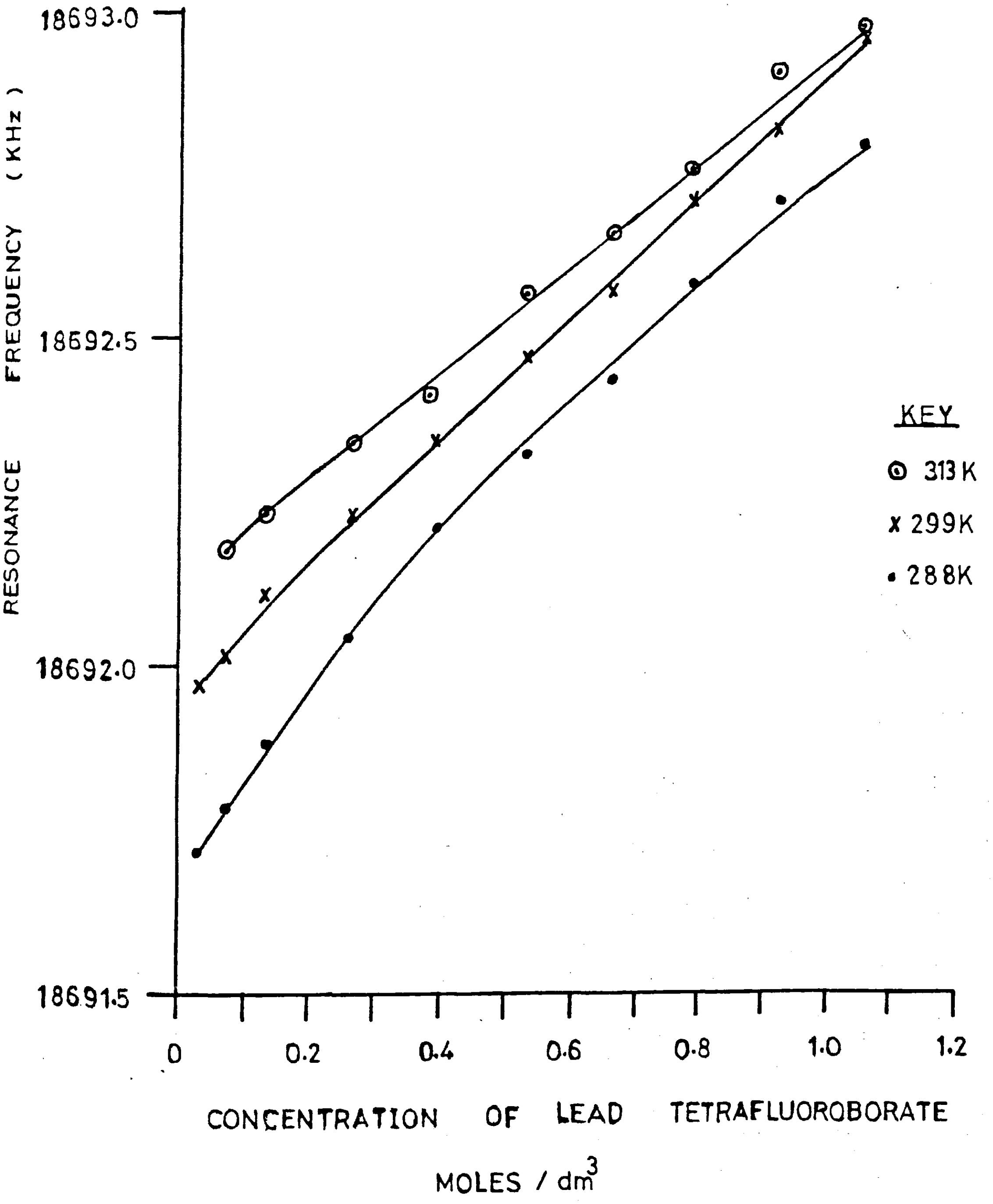


Table 3.4: Chemical Shift of an Acidic Solution of Lead Acetate

This experiment was carried out to investigate the changes in the ^{207}Pb signal by changing the concentration of a series of acidic lead acetate solutions at six different temperatures, in water with added D_2O (V:V $H_2O:D_2O$ 95%:5%)

Temperature (K)	Concentration Lead Acetate (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
278	1.000	18719.210	1476.6
278	0.850	18719.150	1473.4
278	0.650	18718.980	1464.3
278	0.500	18718.600	1443.9
278	0.400	18718.300	1427.9
278	0.300	18717.750	1398.5
278	0.250	18717.450	1382.4
278	0.200	18717.090	1363.2
278	0.100	18714.400	1219.3
278	0.050	18713.000	1144.4
288	1.000	18719.560	1491.6
288	0.850	18719.480	1487.3
288	0.650	18719.300	1477.7
288	0.500	18749.030	1463.3
288	0.400	18718.655	1443.2
288	0.300	18718.250	1421.5
288	0.250	18717.800	1397.4
288	0.200	18717.400	1376.0
288	0.100	18715.585	1278.9
288	0.050	18713.310	1157.2

Table 3.4 (continued)

Temperature (K)	Concentration Lead Acetate (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
299	1.000	18720.215	1526.1
299	0.850	18720.135	1521.8
299	0.650	18719.890	1508.7
299	0.500	18719.555	1490.8
299	0.400	18719.225	1473.1
299	0.300	18718.720	1446.1
299	0.250	18718.330	1425.2
299	0.200	18717.865	1400.4
299	0.100	18716.050	1303.3
299	0.050	18713.835	1184.8
299	0.010	18706.080	769.9
299	0.0010	18700.100	449.9
313	1.000	18720.735	1538.3
313	0.850	18720.880	1546.1
313	0.650	18720.420	1521.5
313	0.500	18720.255	1512.6
313	0.400	18719.995	1498.7
313	0.300	18719.500	1472.2
313	0.250	18718.850	1437.5
313	0.200	18718.640	1426.2
313	0.100	18716.575	1315.8
313	0.050	18714.650	1212.8

Table 3.4 (continued)

Temperature (K)	Concentration Lead Acetate (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
333	1.000	18722.120	1598.5
333	0.850	18722.085	1596.6
333	0.650	18721.815	1582.2
333	0.500	18721.450	1562.6
333	0.400	18720.785	1527.1
333	0.300	18720.250	1497.9
333	0.250	18720.240	1498.4
333	0.200	18719.545	1460.7
333	0.100	18717.730	1363.6
333	0.050	18715.650	1252.3
353	1.000	18723.300	1653.3
353	0.850	18723.200	1647.9
353	0.650	18722.950	1634.6
353	0.500	18722.590	1615.3
353	0.400	18722.230	1576.1
353	0.300	18721.780	1572.0
353	0.250	18721.380	1550.6
353	0.200	18721.020	1531.3
353	0.100	18719.240	1436.1
353	0.050	18718.800	1412.6

GRAPH 3.4

GRAPH OF RESONANCE FREQUENCY CHANGING WITH CONCENTRATION AND TEMPERATURE FOR A SERIES OF ACIDIC LEAD ACETATE SOLUTIONS

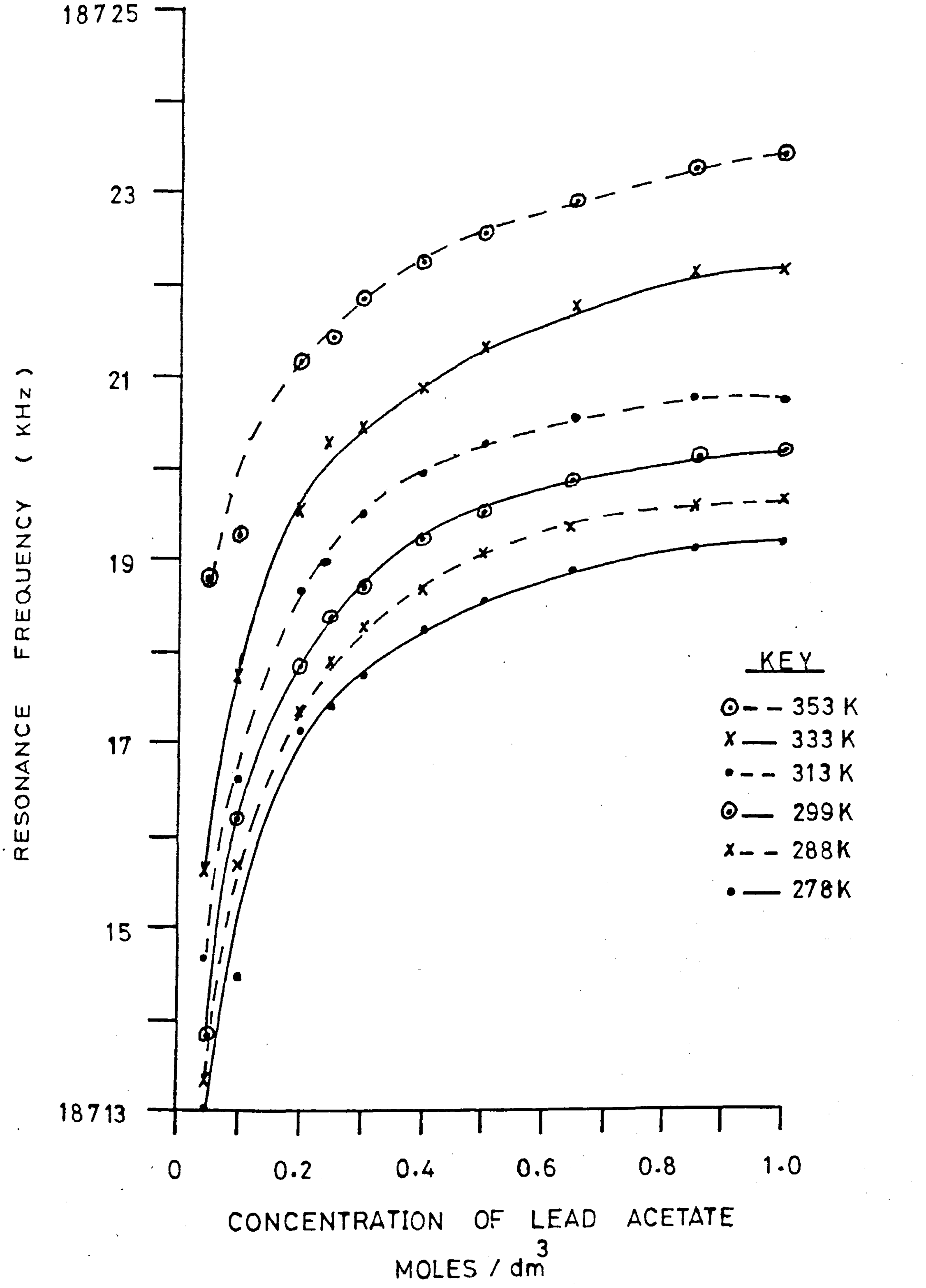


Table 3.5: Lead Nitrate in Acid Solution

These experiments were carried out to show the effect of changing the temperature and concentration for a series of acid lead nitrate solutions (V:V D_2O:H_2O 5%:95%) at pH 1.0.

Temperature (K)	Concentration Lead Nitrate (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
277	1.000	18689.570	-103.1
277	0.850	18689.630	-105.9
277	0.650	18689.800	- 96.8
277	0.500	18689.950	- 88.8
277	0.400	18690.045	- 83.7
277	0.300	18690.220	- 74.4
277	0.250	18690.320	- 69.0
277	0.200	18690.380	- 65.8
277	0.100	18690.660	- 50.8
277	0.050	18690.830	- 41.7
288	1.000	18689.940	- 93.1
288	0.850	18690.053	- 87.0
288	0.650	18690.110	- 83.9
288	0.500	18690.264	- 75.8
288	0.400	18690.370	- 70.1
288	0.300	18690.517	- 62.2
288	0.250	18690.695	- 52.7
288	0.200	18690.700	- 57.8
288	0.100	18690.910	- 41.2
288	0.050	18691.075	- 32.4

Table 3.5 (continued)

Temperature (K)	Concentration Lead Nitrate (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
299	1.000	18690.158	- 81.9
299	0.850	18690.258	- 76.6
299	0.650	18690.415	- 68.2
299	0.500	18690.566	- 60.1
299	0.400	18690.675	- 54.3
299	0.300	18690.835	- 45.7
299	0.250	18690.920	- 41.2
299	0.200	18691.000	- 36.9
299	0.100	18691.220	- 25.1
299	0.050	18691.309	- 20.4
299	0.010	18691.465	- 12.0
299	0.0050	18691.520	- 9.1
313	1.000	18690.570	- 75.4
313	0.850	18690.655	- 70.9
313	0.650	18690.805	- 62.9
313	0.500	18690.945	- 55.4
313	0.400	18691.055	- 49.5
313	0.300	18691.160	- 43.9
313	0.250	18691.230	- 40.1
313	0.200	18691.300	- 36.4
313	0.100	18691.500	- 25.7
313	0.050	18691.850	- 6.9

Table 3.5 (continued)

Temperature (K)	Concentration Lead Nitrate (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
333	1.000	18691.030	- 64.7
333	0.850	18691.100	- 60.9
333	0.650	18691.205	- 55.4
333	0.500	18691.330	- 48.5
333	0.400	18691.420	- 43.9
333	0.300	18691.550	- 36.9
333	0.250	18691.595	- 34.5
333	0.200	18691.675	- 30.2
333	0.100	18691.850	- 20.9
333	0.050	18692.050	- 10.2

GRAPH 3.5

GRAPH OF RESONANCE FREQUENCY CHANGING WITH CONCENTRATION AND TEMPERATURE FOR A SERIES OF ACIDIC LEAD NITRATE SOLUTIONS

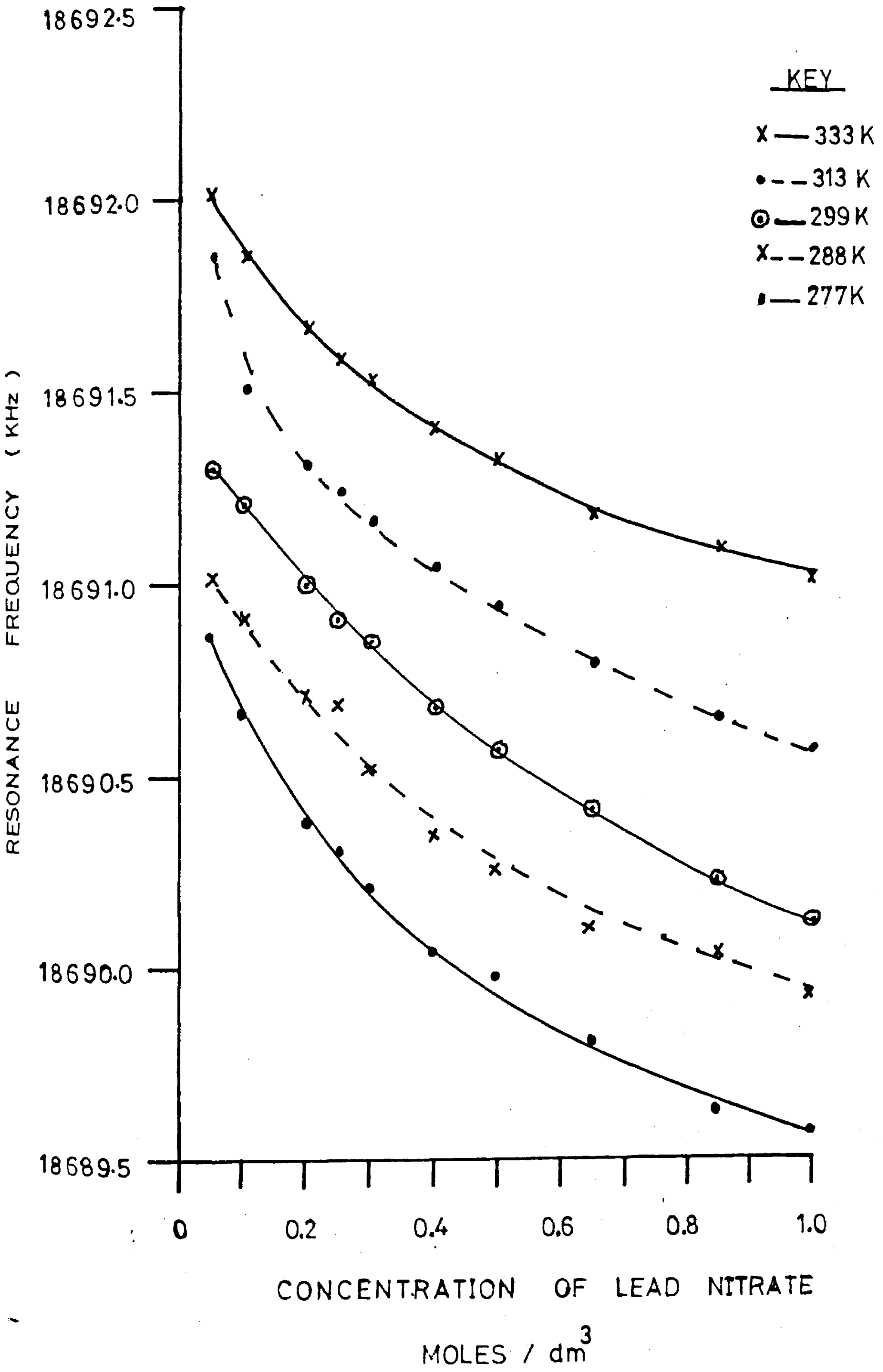


Table 3.6: Lead Nitrate in Alkaline Solution

It was extremely difficult to dissolve lead nitrate in an alkaline solution. Various concentrations of sodium hydroxide were used in the attempt to dissolve the lead salt and 8m sodium hydroxide was found to be the only suitable concentration. Only very dilute lead solutions could be made up, as more concentrated lead nitrate solutions led to precipitation of hydrated lead oxides. Little variation in frequency was found.

Temperature (K)	Concentration Lead Nitrate (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
288	0.050	18765.700	3960.0
288	0.040	18765.770	3963.7
288	0.0250	18765.720	3961.1
288	0.020	18765.800	3965.4
288	0.010	18765.790	3964.8
299	0.100	18765.860	3968.0
299	0.050	18765.825	3966.2
299	0.040	18765.905	3970.4
299	0.0250	18765.835	3966.7
299	0.020	18765.925	3971.5
299	0.010	18765.895	3969.9
299	0.0050	18765.890	3969.6
299	0.0010	18765.950	3972.8
313	0.040	18765.960	3957.8
313	0.0250	18765.900	3954.6
313	0.010	18765.950	3957.3

Table 3.7: Investigation of the ^{207}Pb signal with adding lead perchlorate to a constant concentration of lead nitrate in the presence of acid and D_2O

Temperature (K)	Concentration Lead Nitrate (mol/dm^3)	Concentration Lead Perchlorate (mol/dm^3)	Percentage of D_2O present in solution (mol/dm^3)	Concentration of Acid (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
299	1	0.05	0.05	0.05	18690.255	-76.8
299	1	0.11	0.05	0.05	18690.317	-73.4
299	1	0.22	0.05	0.05	18690.460	-65.8
299	1	0.32	0.05	0.05	18690.562	-60.3
299	1	0.43	0.05	0.05	18690.691	-53.4

Table 3.8: Mixtures of Lead Perchlorate and Lead Nitrate in Acidic Solution

This experiment was carried out to investigate changes in the ^{207}Pb resonance frequency with changing concentration of Pb^{2+} TOTAL, but maintaining a constantratio of 1:2 for the nitrate:perchlorate ligand concentration at three different temperatures.

Table showing content of each solution

Solution Number	Pb^{2+} TOTAL mol/dm^3	Concentration of Lead Perchlorate mol/dm^3	Concentration of Lead Perchlorate mol/dm^3
1f	0.10	0.066	0.033
2f	0.30	0.20	0.10
3f	0.50	0.33	0.16
4f	0.60	0.40	0.20
5f	1.00	0.66	0.33

Table showing chemical shift measurements

Temperature (K)	Solution Number	Resonance Frequency (KHz)	Chemical Shift (ppm)
288	1f	18691.900	11.8
288	2f	18691.755	4.0
288	3f	18691.730	-2.7
288	4f	18691.720	-2.1
288	5f	18691.710	1.6

Table 3.8

Table showing chemical shift measurements (continued)

Temperature (K)	Solution Number	Resonance Frequency (KHz)	Chemical Shift (ppm)
299	1f	18692.020	17.6
299	2f	18691.865	9.4
299	3f	18691.830	7.5
299	4f	18691.830	7.5
299	5f	18691.815	6.7
313	1f	18692.170	10.2
313	2f	18692.045	3.5
313	3f	18692.025	2.4
313	4f	18692.020	2.1
313	5f	18692.010	1.6

GRAPH 3.8

GRAPH OF RESONANCE FREQUENCY vs LEAD CONCENTRATION FOR ACIDIC MIXTURES OF LEAD PERCHLORATE AND LEAD NITRATE AT VARIOUS TEMPERATURES

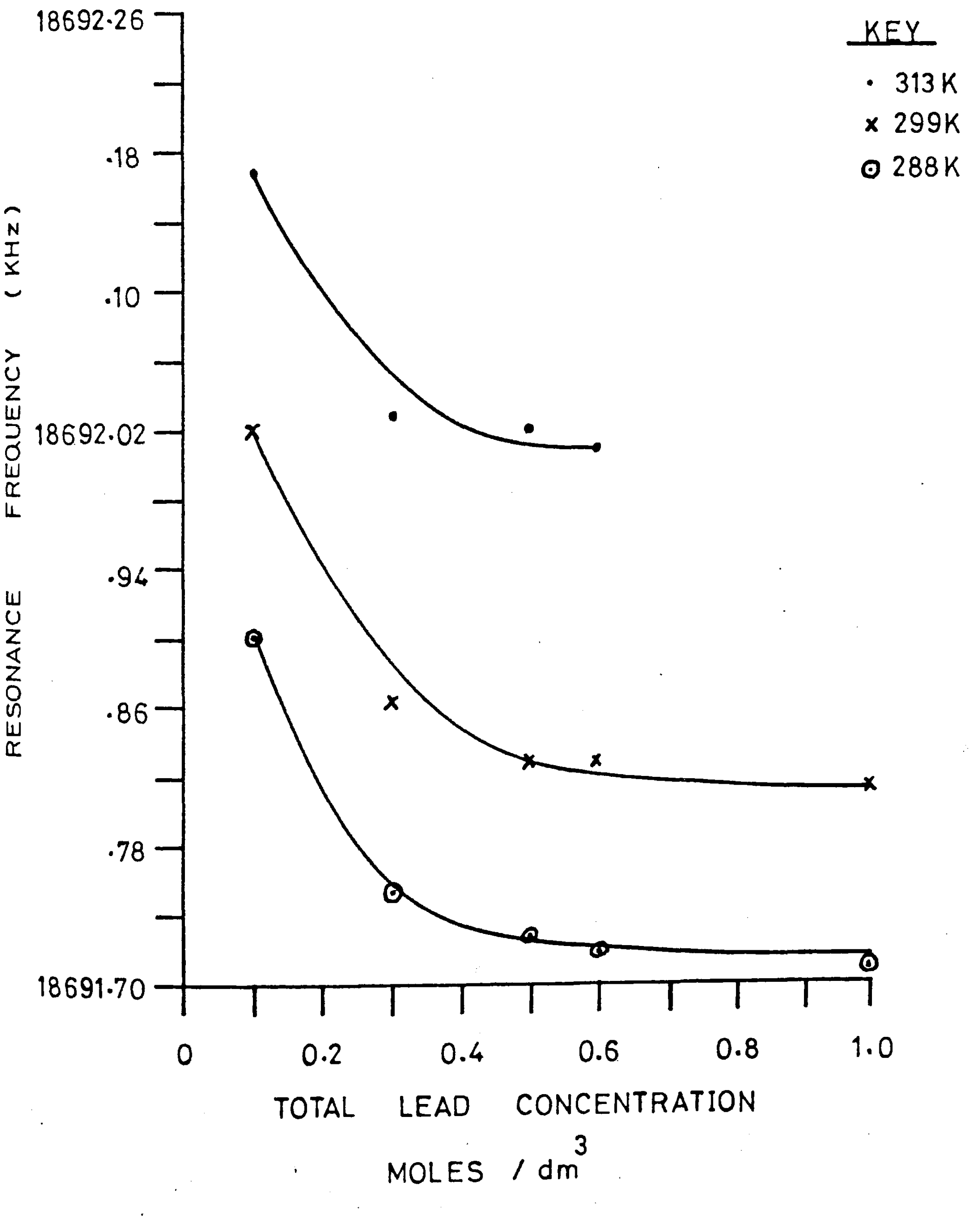


Table 3.9: Mixtures of Lead Perchlorate, Sodium Perchlorate, Sodium Acetate in Acid Solution

The following tables show the results from experiments, using mixtures of lead perchlorate, sodium perchlorate, sodium acetate in acid solution. This experiment was carried out to investigate the changing position of the ^{207}Pb signal using constant lead concentration, excess perchlorate ligand and increasing the acetate ligand.

Table to show composition of each solution

Solution Number	Concentration of Components in Mixture in mol/dm^3 Concentration of Lead Perchlorate	Concentration of Sodium Perchlorate	Concentration of Sodium Acetate
1d	1.00	1.95	0.05
2d	1.00	1.93	0.07
3d	1.00	1.90	0.10
4d	1.00	1.88	0.12
5d	1.00	1.85	0.15
6d	1.00	1.80	0.20
7d	1.00	1.50	0.50
8d	1.00	1.25	0.75
9d	1.00	1.0	1.00
10d	1.00	0.75	1.25
11d	1.00	0.50	1.50
12d	1.00	0.25	1.75
13d	1.00	0.00	2.00

Table 3.9 (continued)

Temperature (K)	Solution Number	Resonance Frequency (KHz)	Chemical Shift (ppm)
288	1d	18694.210	135.3
288	2d	18694.300	143.9
288	3d	18694.440	147.6
288	4d	18694.710	162.1
288	5d	18694.950	178.7
288	6d	18695.450	205.4
288	7d	18698.790	380.3
288	8d	18701.650	537.1
288	9d	18704.680	695.5
288	10d	18706.720	804.6
288	11d	18709.480	952.3
288	12d	18711.480	1059.3
288	13d	18713.450	1164.7
299	1d	18694.080	127.9
299	2d	18694.350	142.3
299	3d	18694.505	150.6
299	4d	18694.760	164.2
299	5d	18695.100	182.4
299	6d	18695.600	209.2
299	7d	18699.080	395.4
299	8d	18701.800	540.9
299	9d	18705.100	717.4
299	10d	18707.310	835.7

Table 3.9 (continued)

Temperature (K)	Solution Number	Resonance Frequency (KHz)	Chemical Shift (ppm)
299	11d	18710.090	984.4
299	12d	18712.070	1090.3
299	13d	18714.135	1200.8
313	1d	18694.155	116.4
313	2d	18694.500	134.8
313	3d	18694.585	139.4
313	4d	18694.850	153.5
313	5d	18695.400	182.9
313	6d	18695.900	209.7
313	7d	18699.320	392.7
313	8d	18702.500	562.8
313	9d	18705.420	719.0
313	10d	18707.720	842.1
313	11d	18710.480	989.7
313	12d	18712.580	1102.1
313	13d	18714.650	1212.8

GRAPH 3.9

GRAPH OF ^{207}Pb RESONANCE FREQUENCY vs ACETATE CONCENTRATION FOR ACIDIC MIXTURES OF LEAD PERCHLORATE, SODIUM PERCHLORATE AND SODIUM ACETATE AT VARIOUS TEMPERATURES

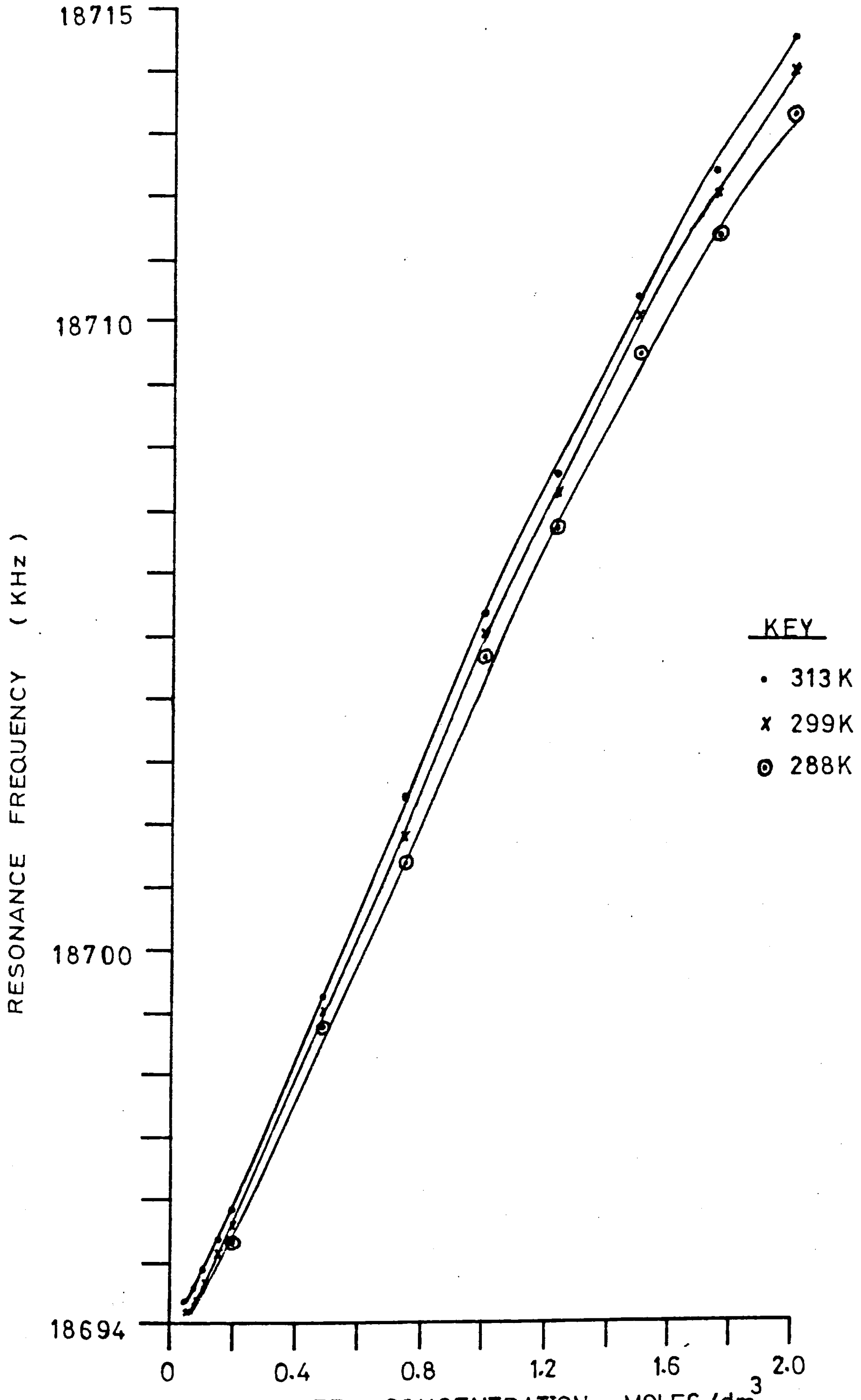


Table 3.10: The effect of adding nitrate ion in the form of nitric acid to lead nitrate, on the ^{207}Pb resonance signal at 299K

Concentration of Lead Nitrate (mol/dm^3)	Concentration of Nitric Acid (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
1.00	1.00	18689.660	-108.6
1.00	0.05	18690.158	- 81.9
1.00	0.00	18690.660	- 55.1
0.50	1.00	18689.978	- 91.6
0.50	0.50	18690.200	- 79.7
0.50	0.10	18690.470	- 65.3
0.50	0.05	18690.520	- 62.6
0.50	0.00	18690.625	- 56.9
0.25	1.00	18690.090	- 85.6
0.25	0.05	18690.920	- 41.2
0.25	0.00	18690.930	- 40.7
0.10	0.10	18691.160	- 28.4
0.10	0.005	18691.220	- 25.1
0.10	0.00	18691.275	- 22.2

Table 3.11: Changes in ^{207}Pb signal with the addition of nitrate ion in the form of sodium nitrate

This experiment was carried out using mixtures of lead perchlorate, sodium perchlorate and sodium nitrate, in acid solution, to investigate the changes in the ^{207}Pb resonance signal with changing the nitrate ion concentration at pH 1.50.

The following table shows the composition of each solution.

Solution Number	Concentration of Lead Perchlorate (mol/dm^3)	Concentration of Sodium Perchlorate mol/dm^3)	Concentration of Sodium Nitrate (mol/dm^3)
1e	1.00	1.950	0.050
2e	1.00	1.925	0.075
3e	1.00	1.900	0.100
4e	1.00	1.875	0.125
5e	1.00	1.850	0.150
6e	1.00	1.800	0.200
7e	1.00	1.500	0.500
8e	1.00	1.250	0.750
9e	1.00	1.000	1.000
10e	1.00	0.750	1.250
11e	1.00	0.500	1.500
12e	1.00	0.250	1.750
13e	1.00	0.000	2.000

Table 3.11 (continued)

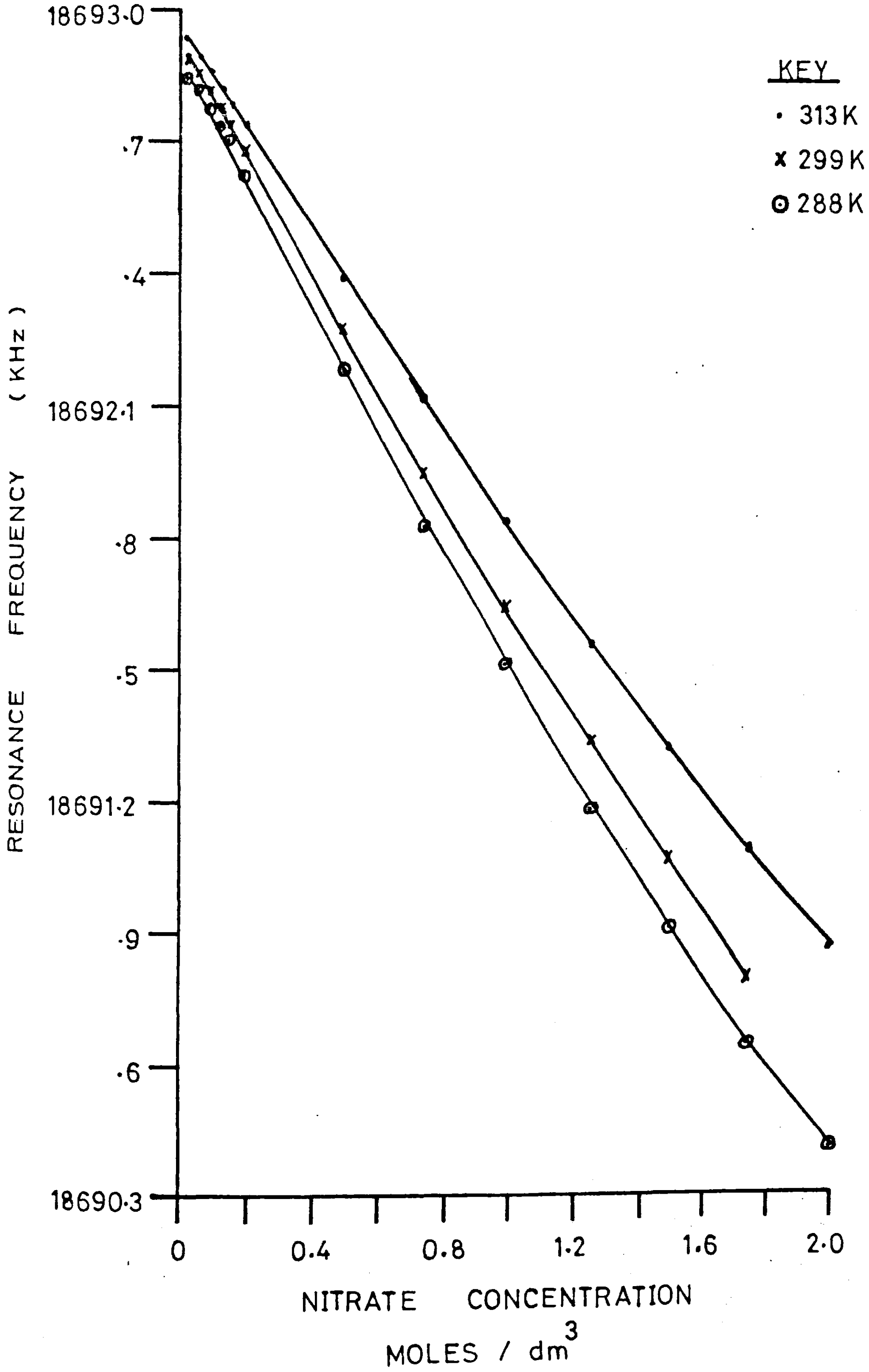
Temperature (K)	Solution Number	Resonance Frequency (KHz)	Chemical Shift (ppm)
288	1e	18692.840	62.1
288	2e	18692.820	61.0
288	3e	18692.775	58.6
288	4e	18692.730	56.2
288	5e	18692.700	54.6
288	6e	18692.625	50.6
288	7e	18692.185	27.0
288	8e	18691.820	7.5
288	9e	18691.510	- 9.1
288	10e	18691.190	-26.2
288	11e	18690.900	-41.7
288	12e	18690.640	-55.6
288	13e	18690.390	-69.0
299	1e	18692.888	64.1
299	2e	18692.845	61.8
299	3e	18692.810	59.9
299	4e	18692.765	57.5
299	5e	18692.730	55.6
299	6e	18692.665	52.2
299	7e	18692.260	30.5
299	8e	18692.945	13.6
299	9e	18691.640	- 2.7

Table 3.11 (continued)

Temperature (K)	Solution Number	Resonance Frequency (KHz)	Chemical Shift (ppm)
299	10e	18691.335	-19.0
299	11e	18691.060	-33.7
299	12e	18690.800	-47.6
299	13e	18690.575	-59.7
313	1e	18692.920	50.3
313	2e	18692.875	47.9
313	3e	18692.860	47.1
313	4e	18692.825	45.2
313	5e	18692.790	43.3
313	6e	18692.740	40.7
313	7e	18692.390	21.9
313	8e	18692.110	7.0
313	9e	18691.835	- 7.8
313	10e	18691.560	-22.5
313	11e	18691.325	-35.0
313	12e	18691.090	-47.6
313	13e	18690.865	-59.7

GRAPH 3.11

GRAPH OF ^{207}Pb RESONANCE FREQUENCY vs NITRATE CONCENTRATION FOR ACIDIC MIXTURES OF LEAD PERCHLORATE, SODIUM PERCHLORATE AND SODIUM NITRATE AT VARIOUS TEMPERATURES



Lead with Thiourea, EDTA and Urea

The following experiments were carried out to investigate the effect of thiourea, urea and EDTA on the ^{207}Pb signal.

Various difficulties were encountered in measuring the ^{207}Pb signal. Only very dilute lead solutions (usually 0.05 mol/dm^3) could be investigated, as more concentrated solutions resulted in solid complexes being precipitated. Also most of the experiments had to be carried out at a temperature of 313K, otherwise the complexes present would not remain in solution.

An inner capillary of deuterium oxide was used inside the 10mm NMR sample tube as the locking material for these experiments.

Table 3.12: Lead Nitrate with EDTA at 299K

Nature of Solution	Concentration Lead Nitrate (mol/dm^3)	Concentration EDTA (mol/dm^3)	Concentration Nitric Acid (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
Acidic	0.50	0.02	0.20	18691.540	- 8.0
Acidic	0.50	0.025	0.20	18690.695	- 53.2
Acidic	0.50	0.05	0.20	18690.763	- 49.6
Acidic	1.00	0.12	0.00	18730.505	2076.6
Acidic	0.09	0.11	0.00	18732.910	2205.3
Neutral	0.09	0.11	0.00	18732.115	2162.7
Acidic	0.09	0.11	0.20	18730.048	2052.1
Alkaline	0.09	0.11	0.00	18734.242	2276.5
	0.17	0.10	0.00	18730.120	2058.1

Table 3.13: The effect of adding small amounts of EDTA to a stock solution of acidic 1 mol/dm^3 lead nitrate solution

Temperature (K)	Weight of added EDTA in 10 cm^3 Total Volume (g)	Resonance Frequency (KHz)	Chemical Shift (ppm)
288	0.01	18689.771	-102.1
288	0.05	18689.905	- 95.0
288	0.10	18690.127	- 83.1
299	0.01	18690.219	- 78.7
299	0.05	18690.387	- 69.7
299	0.10	18690.579	- 59.4
333	0.01	18691.329	- 48.7
333	0.05	18691.178	- 56.8
333	0.10	18690.936	- 69.8

Table 3.14: Lead Nitrate and EDTA

Concentration Lead Nitrate (mol/dm^3)	Concentration EDTA (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)	pH
0.05	0.05	18735.280	2332.05	6.50
0.10	0.10	18735.120	2323.49	6.00
0.30	0.01	18735.120	2323.49	5.50

Table 3.15: Lead Oxide and Nitrate with EDTA at 299K

Lead Compound	Concentration Lead Compound (mol/dm^3)	Concentration EDTA (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)	Linewidth (Hz)	pH
Lead Oxide	0.025	0.03	18735.230	2329.4	100	5.80
Lead Nitrate	0.025	0.03	18735.029	2318.6	100	3.46
Lead Oxide	0.025	0.11	18735.280	2332.1	100	6.16
Lead Nitrate	0.049	0.045	18721.998	1621.5	80	4.52

Table 3.16: Lead Nitrate with EDTA and Thiourea

Temperature - (K)	Concentration Lead Nitrate (mol/dm^3)	Concentration EDTA (mol/dm^3)	Concentration Thiourea (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
299	0.05	0.04	0.06	18732.096	2161.7
299*	0.10	0.05	0.36	18731.208	2114.2
299*	0.10	0.05	0.36	18716.829	1344.9
313	0.05	0.04	0.06	18732.270	2155.5

* Two separate signals have been observed for ^{207}Pb resonance signal in one solution.

Table 3.17: Lead Nitrate with Thiourea at 313K

Solution Number	Concentration Lead Nitrate (mol/dm^3)	Concentration Thiourea (mol/dm^3)
1	0.05	0.00
2	0.05	0.05
3	0.05	0.10
4	0.05	0.16
5	0.05	0.20
6	0.05	0.30

Solution Number	Resonance Frequency (KHz)	Chemical Shift (ppm)	Linewidth (Hz)	pH
1	18690.642	- 71.6	5	1.98
2	18693.669	90.4	5	2.31
3	18693.669	219.0	10	1.62
4	18698.892	369.8	50	2.02
5	18701.969	534.4	60	2.35
6	18711.626	1051.1	70	3.76

Table 3.18: Lead with Urea and Thiourea at 299K

pH	Lead Compound	Concentration Lead Compound (mol/dm^3)	Ligand	Concentration of Ligand (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
4.83	Lead Nitrate	0.05	Urea	0.3	18691.500	- 10.2
1.98	Lead Tetrafluoroborate	0.05	Thiourea	0.3	18710.949	1030.1
3.76	Lead Nitrate	0.05	Thiourea	0.3	18714.700	1231.0

Table 3.19: Lead Nitrate with Added Citric Acid

Citric acid in various known amounts was added to an acidic solution of lead nitrate (1 mol/dm^3) at 299K, and the change in ^{207}Pb resonance signal was observed.

Concentration Lead Nitrate mol/dm^3	Weight of added Citric Acid (g)	Resonance Frequency (KHz)	Chemical Shift (ppm)
1.00	0.2000	18690.948	-39.7
1.00	0.1000	18690.707	-52.6
1.00	0.0500	18690.526	-62.3
1.00	0.0100	18690.304	-74.2

All samples were of 10 cm^3.

Table 3.20: Lead Nitrate with Ascorbic Acid

Ascorbic acid in various known amounts was added to an acidic solution of lead nitrate (1 mol/dm^3) at 299K and the change in the ^{207}Pb signal was observed.

Concentration Lead Nitrate mol/dm^3	Weight of Ascorbic Acid (g)	Resonance Frequency (KHz)	Chemical Shift (ppm)
1.00	0.2000	18690.251	-77.0
1.00	0.1000	18690.199	-79.8
1.00	0.0500	18690.190	-80.3
1.00	0.0100	18690.159	-82.0

All samples were of 10cm^3.

Table 3.21: Lead Nitrate with Anthranilic Acid

Solution Number	Anthranilic Acid (mol/dm^3)	Concentration of Pb^{2+} (mol/dm^3)
1	0.49	0.95
2	1.96	0.78
3	3.76	0.60
4	5.29	0.40
5	7.05	0.20

Temperature (K)	Solution Number	Resonance Frequency (KHz)
288	1	18689.910
288	2	18690.010
288	3	18690.180
288	4	18690.400
288	5	18690.730
299	1	18690.180
299	2	18690.325
299	3	18690.490
299	4	18690.725
299	5	18691.045
313	1	18690.485
313	2	18690.650
313	3	18690.815
313	4	18691.020
313	5	18691.300

Table 3.22: Lead Compounds with various different ligands

The following experiments were carried out to investigate the effect on ^{207}Pb signal of adding known amounts of different ligands to a known concentration of a lead salt. All the experiments were carried out at 299K.

Lead Salt	Concentration of Lead Salt (mol/dm^3)	Ligand	Concentration of Ligand (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
Lead Nitrate	0.50	Ethylenediamine	0.50	18745.137	2859.4
Lead Nitrate	0.251	Ethylenediamine	0.75	18750.150	3127.6
Lead Perchlorate	0.50	Ethanolamine	Saturated Solution	18692.290	32.1
Lead Nitrate	0.66	Triethylenetetramine	0.33	18748.330	3030.2
Lead Nitrate	0.75	Triethylenetetramine	0.25	18748.611	3045.3
Lead Acetate	0.50	Triethanolamine	0.50	18740.629	2618.2
Lead Nitrate	0.75	Triethanolamine	0.25	18690.050	- 87.7
Lead Acetate	1.00	Sulphamic Acid	Saturated Solution	18717.972	1406.1
Lead Nitrate	1.00	Sulphamic Acid	Saturated Solution	18690.240	- 77.6

Table 3.23: ^{207}Pb resonance signal for a variety of lead compounds using various solvents

The following table shows the ^{207}Pb resonance frequency signal referenced to lead perchlorate at infinite dilution at stated temperatures, for a variety of lead complexes.

These experiments were carried out to indicate the range of chemical shift values that can be obtained for ^{207}Pb resonance signal.

Temperature (K)	Complex	Solvent	Resonance Frequency (KHz)	Chemical Shift (ppm)	Conditions	Source of Sample
299	Lead Tetraacetate	$CDCl_3$ + TMS	18710.637	1013.66	No decoupling Sharp peak Saturated solution	Hopkin & Williams Ltd.
303	Hexaphenyl Dilead	C_6D_6	18744.380	2818.89	Completely decoupled Saturated Solution	ABC Chemicals
299	Lead Diethyl-dithiocarbamate	CD_2Cl_2	18755.430	3410.07	No decoupling	Fluka
		$CDCl_3$	18755.250	3400.44	Saturated solution in both solvents	
299	Trinormal Propylplumbyl Acetate	C_6D_6	18752.330	3244.22	Saturated Solution	ABC Chemicals

Table 3.23 (continued)

Temperature (K)	Complex	Solvent	Resonance Frequency (KHz)	Chemical Shift (ppm)	Conditions	Source of Sample
299	Triphenylplumbyl Acetate	C_6D_6	18750.280	3134.55	Saturated Solution	ABC Chemicals
303	Lead Tetramethyl	15% MePh 30% C_6D_6	18745.725	2890.86	Completely decoupled	Dr. W. MacFarlane at City Polytechnic
299	Lead Dithionate	H_2O/D_2O	18692.100	21.935	No decoupling 0.195m sol'n	Prepared
299	Lead Thiocyanate	DMSO	18705.000	712.08	Saturated Solution	Aldrich Chemicals
299	Lead Dimethyl-glyoxime	MeOD	18692.885	63.93	Saturated Solution	Prepared
299	Lead Ethyl Cysteine Ester Hydrochloride	HCl (3mol/dm^3)	18734.670	2299.42	Saturated Solution	Prepared
299	Lead Acetylacetone	D_2O/H_2O	18693.050	72.7	Saturated Solution	Prepared
299	Lead Sulphamate	D_2O/H_2O	18717.972	1406.00	Saturated Solution	Prepared

3.5 Preparations

a) Lead Dithionate

A sample of lead dithionate was prepared by weighing out a known amount of potassium dithionate exactly and dissolving it in a small quantity of water. The solution was then washed on to an ion exchange column in the acid form and washed through with water. The solution from the column was collected in a beaker containing lead carbonate. Effervescence occurred as the dithionic acid from the column reacted with the lead carbonate to produce a solution of lead dithionate. When effervescence had ceased, the solution was filtered and then made up to a known volume with water. By considering the capacity of the column material an estimation of the concentration of the lead dithionate solution could be made. The solution was then analysed to determined the exact lead concentration.

b) Lead ethyl cysteine ester hydrochloride[78]

Bis (ethyl L-cysteineato) lead II

Cysteine ester hydrochloride (0.01 mole), sodium hydroxide (0.02 mole) and lead nitrate (0.005 mole) were used for this experiment. The ester was dissolved in water (10 ml) and then the solution was cooled to 0°C. Ice cold sodium hydroxide in water (10 ml) was added to the ester solution, and then a solution of lead nitrate in water (10 ml) was added and the mixture was vigorously stirred. A yellow precipitate formed immediately but on stirring the precipitate dissolved and precipitation of a colourless crystalline solid occurred. This was the desired product. The complex was collected, washed with alcohol and water and dried in vacuum over phosphorus pentoxide. The NMR spectrum of this compound was taken immediately because the compound was found to decompose rapidly to a black oily material within a period of one week.

c) Lead Acetylacetone[79]

Lead acetylacetone was prepared by adding lead oxide (22g) to acetylacetone (20g). The mixture was then boiled with toluene, which was partly distilled off until the distillate was no longer cloudy. This removed the water formed by the reaction. The mixture was filtered, and a solid separated on cooling. The solid was recrystallised from toluene containing a little acetylacetone.

d) Lead Sulphamate

This complex was prepared by mixing lead nitrate (0.1 mole) in water with sulphamic acid (0.1 mole).

e) Lead Dimethylglyoxime

Dimethylglyoxime (4.6g in 30 cm^3 of 2.5 mol/dm^3 sodium hydroxide), water (20 cm^3) and lead nitrate (6.6g in 25 cm^3 water) were mixed together. Precipitation occurred and the solid was filtered, washed with water (4 x 10 cm^3) and dried.

3.6 Introduction to Discussion

The NMR chemical shift data obtained in the experimental sections of Chapters 3 and 4 indicate that the major factor in the position of the resonance signal for ^{113}Cd and ^{207}Pb is the immediate chemical environment around the nucleus. A cation generally will only give one resonance signal, except under very unusual circumstances. In principle a system containing a solvated metal cation, solvated anion and bulk solvent, could give several resonances due to the cation. To permit the observation of separate signals, the nucleus under investigation must remain in a particular environment for a time greater than the reciprocal of the frequency of the NMR signal, the time being of the order of milliseconds. The nucleus obviously undergoes exchange between the different possible environments and this exchange may be either fast or slow.

For fast exchange, the observed chemical shift will depend upon the concentration of the salt solution as the time each solvent molecule spends under the influence of an anion or cation depends on the ratio of the bulk solvent to the solvating solvent.

For slow exchange, the cation primary solvation resonance is constant, but the signal area changes with concentration.

When a graph of chemical shift vs. concentration for a particular salt is plotted and the graph is non-linear, then ion-pairing or complex formation is indicated.

A small quantity of a known concentration of acid was added to some samples investigated for chemical shift changing with concentration and temperature, as these experiments carried out with no acid present, gave slightly less reliable results than the same experiments carried out with a little acid added to the solution. The trace of acid was present in order to suppress hydrolysis. The first equilibrium for the hydrolysis of Pb^{2+} (aqueous) may be written as:

$$Pb^{2+}\ (aq) + H_2O \rightleftharpoons Pb\ (OH)^+ + OH^-\ (aq) \qquad K = 10^{-8}\ mol^{-1}\ dm^3$$

Under these conditions, even with 0.05 mol dm^{-3} acid present, the hydrolysis is extremely small.

In the following sections, all the tabulated results and graphs in Chapter 3 are discussed in some detail.

3.7 Lead Perchlorate in Acid Solution

The chemical shift measurements of these solutions did show a change with both temperature and concentration. These changes are shown in graph 3.1.

The highest resonance frequency signal for a particular concentration was found to occur at the highest temperature. Also the more concentrated the solution at a given temperature, the higher the resonance frequency.

The graph plots linking these changes were thought to be accurate enough to extrapolate the lines to infinite dilution where the lead may exist as $Pb(H_2O)n^{2+}$. This value, at particular temperatures, was used to reference all the ^{207}Pb chemical shift data and for the model to calculate some equilibrium constant, K, values (Chapter 5) for lead nitrate in acidic solution.

The change in the resonance frequency with concentration in this case was probably due to effects such as bulk susceptibility changes because of the ionic concentration. These effects should be similar for all the solutions. The initial low field shift may be due to longer range interactions between the anion and the Pb^{2+} hydration sphere.

Generally, ion pairs are thought not to form in perchlorate dilute solutions.[118]

The linewidths of the perchlorate solutions have been found to be narrow (about 10 Hz) at room temperature and moderate concentrations, but broad lines can be obtained at high concentrations, this is probably due to the viscosity of the solution.

3.8 The effect of pH on ^{207}Pb signal in 0.23 mol/dm^3 acidic lead perchlorate

The pH of the solutions studied could be altered only up to pH 5. Above pH 5, precipitation of various hydroxides of lead occurred. The pH of the solutions was controlled by adding either sodium hydroxide or perchloric acid. The value of the chemical shift was found to increase by 10 ppm by changing the pH from 1.0 to 4.0, so the pH of the medium will slightly alter the chemical shift data, here presumably due to hydrolysis.

3.9 Lead tetrafluoroborate in acid solution

The shape of the plot for a graph of resonance frequency of ^{207}Pb signal vs. concentration at various temperatures (graph 3.3) was similar to the graph obtained for the lead perchlorate experiment (graph 3.1). Lead tetrafluoroborate is thought to behave in a similar way to lead perchlorate in solution, i.e. no significant ion-pairing in dilute solutions.

3.10 Lead nitrate in acid solution

The value of the resonance frequency of ^{207}Pb signal was found to increase with increasing temperature at a particular concentration. This trend was found to be the same as for the lead perchlorate solutions.

The value of the resonance frequency was found to decrease with increasing concentration at a particular temperature for the nitrate solutions. This was the opposite result to the perchlorate trend. Also all the resonances due to ^{207}Pb in lead nitrate occurred at a lower frequency than the ^{207}Pb resonance in lead perchlorate, and all the other lead complexes investigated.

Lead nitrate is thought to dissociate in water in two steps:

$$Pb(NO_3)_2 \longrightarrow PbNO_3^+ + NO_3^-$$

$$PbNO_3^+ \longrightarrow Pb^{2+} + NO_3^-$$

Aqueous solutions of lead nitrate are stable only below pH 5. The ^{207}Pb resonance signal in acidic lead nitrate may be partly due to the $PbNO_3^+$ ion pair. This concept seems reasonable when it is used as a model to predict equilibrium constant values in Chapter 5. Using the Jeol FX90Q spectrometer, the linewidth of the ^{207}Pb resonance signal was between 5-10 Hz at 299K, about 50 Hz at 278K and about 10 Hz at 333K. Some peak splitting was observed at 313K. The splitting may have been due to more than one species being present in the solution under the experimental conditions. Another reason for the splitting may be the temperature gradient within the solution. The latter was thought not to be an explanation for the splittings as careful sample temperature control was ensured at all times and the experiments were repeated several times with similar results being obtained.

3.11 Lead nitrate in alkaline solution

The ^{207}Pb resonance was investigated at several concentrations and at three different temperatures. The concentration ranges available were extremely small i.e. from 0.05 mol/dm^3 to 0.001 mol/dm^3. There was not a definite trend in the resonance frequency values with altering the concentration and temperature. All the values appeared to be at about the same resonance frequency within experimental error. This would suggest that the environment of the lead under these conditions is very similar.

The position of the resonance signal for lead in alkaline lead nitrate solution was very different from the position of the resonance signal for lead in acid lead nitrate solution. The alkaline lead nitrate signal was 3986 ppm away from the corresponding concentration acidic lead nitrate solution signal. Several anions containing Pb(II) have been suggested but no useful trend in resonance frequency could be detected.

3.12 Lead acetate in acid solution

The position of ^{207}Pb resonance signal changed with concentration and temperature in these experiments. The signal increased in resonance frequency with an increase in temperature at a particular concentration. The signal also increased in resonance frequency with an increase in concentration. This was similar behaviour to the lead perchlorate and lead tetrafluoroborate results, although the ^{207}Pb signal in lead acetate (1 mol/dm^3) occurred 1478 ppm away from $Pb(ClO_4)_2$ (1 mol/dm^3) signal i.e. at a higher resonance frequency.

The linewidths of the ^{207}Pb signal for lead acetate solutions are generally broader than the linewidths due to the signal for lead nitrate or lead perchlorate.

3.13 Mixtures of lead perchlorate and lead nitrate in acid solution

The results for these experiments have been tabulated in tables 3.7 and 3.8.

In table 3.7 lead perchlorate was added to a constant concentration of lead nitrate. The resonance frequency of the ^{207}Pb signal increased with adding lead perchlorate. This result may have been due to the increase in lead concentration or the perchlorate ligand may have been shifting the ^{207}Pb signal downfield. From previous data, table 3.1 and table 3.5, it can be seen that the ^{207}Pb resonance signal in lead perchlorate occurs at a higher resonance frequency than the ^{207}Pb resonance signal for lead nitrate (at the same concentration and temperature).

The experimental results in table 3.8 and graph 3.8 show the changes in the ^{207}Pb resonance frequency with changing the total concentration of the lead ion, but maintaining a constant ratio of perchlorate to nitrate ligand. The change in the ^{207}Pb resonance signal in this case should only be due to the changing lead ion concentration. The resonance frequency of the ^{207}Pb signal was found to decrease in value with increasing concentration of Pb^{2+} in solution. The highest frequency signal was found to occur at the highest temperature. This temperature dependence can be seen in table 3.1 for the lead perchlorate results, from these results it appears that the $Pb(H_2O)n^{2+}$ signal at zero concentration varies with temperature in a similar manner. This may be due to a variable hydration effect, as the temperature is altered. Nuclei other than lead for example, cadmium or tin, probably show similar trends.

3.14 Mixtures of lead perchlorate, sodium perchlorate and sodium acetate

The chemical shift of the ^{207}Pb signal increased with the addition of acetate ion and with an increase in temperature. This was expected when these results were compared with the results obtained for lead acetate in acid solution, table 3.4. Graph 3.9 of the resonance frequency vs. acetate concentration gives an almost linear plot.

3.15 The effect of adding nitrate ion to lead nitrate

Nitrate ion was added to lead nitrate solutions as nitric acid, table 3.10, and as sodium nitrate, table 3.11.

Changes of about 10 ppm were obtained with adding nitric acid to a constant concentration of lead nitrate. The resonance frequency of the ^{207}Pb signal was found to increase with adding nitric acid to a constant concentration of aqueous lead nitrate.

Adding sodium nitrate to lead perchlorate solution caused the resonance frequency of the ^{207}Pb signal to decrease with increasing the amount of added nitrate ion. The pH and ionic strengths were constant for all the solutions in the experiment, only the amount of added nitrate ion was altered. The results for this experiment are given in table 3.11. These results show an expected trend in comparison with the results obtained in table 3.5 for acidic solutions of lead nitrate and table 3.1 for acidic solutions of lead perchlorate.

The changes observed when nitric acid was the source of nitrate ion were partly due to pH changes but also largely caused by ion pairing. The chemical shift changes observed by adding nitrate ion were probably due to the formation of the $PbNO_3^+$ ion pair rather more so than any lead perchlorate species or lead surrounded by water species as more nitrate ion was added to the solution, causing the observed ^{207}Pb resonance signal to move towards the expected values for acidic lead nitrate solutions.

3.16 Lead with thiourea, EDTA and urea

The main idea behind this study was to complex Pb^{2+} in aqueous solution with a ligand to give a very stable complex, and then to attempt to obtain a solution containing both Pb^{2+} aqueous and a lead-ligand (Pb-Ln) species to see if the two different signals due to the ^{207}Pb signal in two completely different environments could be obtained under certain circumstances. It was thought that the study would be more successful if a 1:1 complex could be used, with the ligand filling all the coordination positions around the lead. EDTA was thought to be a possible ligand, but problems were encountered with solubility limitations. Conditions can be found where Pb^{2+} aqueous is soluble and separately for PbEDTA (the equilibrium constant for the formation of PbEDTA is about 10^{18}) being soluble in sufficient amounts for NMR signals to be obtained, but it was not found possible to produce conditions where Pb^{2+} (aqueous) and PbEDTA are soluble together, as a solution of PbEDTA requires a pH of not less than around 5 to keep the complex in solution and Pb^{2+} would certainly be hydrolysed under these conditions. It was then decided that maybe if two different ligands were used to maintain the lead in two different environments, two ^{207}Pb signals could be obtained.

Thiourea was introduced into the study to obtain the lead in a different environment from the lead with EDTA.

Urea was introduced to observe whether the lead would coordinate to urea, and if the coordination occurred, where the ^{207}Pb signal would occur in relation to ^{207}Pb signal for lead coordinated to thiourea.

The following sections discuss the results obtained when lead-thiourea, lead-urea, lead-EDTA and lead-thiourea-EDTA systems were investigated.

3.17 Lead with thiourea

In the solid state, lead is thought to combine with thiourea to form PbL_6 (where L represents the ligand thiourea). PbL_6 has been assumed to form to some extent in solution.

Thiourea, when present with lead, in slightly more than six fold excess, has been found to precipitate $Pb[SC(NH_2)_2]_6$ Ln (where Ln can be ClO_4, BF_4 or NO_3) from solutions of moderate concentration. Mixtures of lead salts and thiourea can be maintained in solution if the total lead concentration is no greater than 0.05 mol/dm^3.

Some equilibrium constants for formation of lead-thiourea complexes have been deduced from potentiometric measurements and are reported[80] to be:

$$\left.\begin{array}{ll} K_1 = 4 , & \beta_2 = 11 \\ \beta_3 = 9.5 , & \beta_4 = 110 \end{array}\right\} \begin{array}{l}\text{all in}\\ \text{mol } l^{-1}\\ \text{units}\end{array}$$

at about 298K. No higher stepwise constant (K) or overall formation constant (β) was reported. These figures indicate that a vast excess of thiourea would be required to approach complete replacement of water by the ligand thiourea, at equilibrium in aqueous solution. Possibilities were thought to exist for utilising NMR data to estimate the unknown constants and/or of deducing a lead resonance signal in an all sulphur coordinated environment.

The results are shown in table 3.24 for some solutions studied. The table shows the results of calculated concentrations of various lead-thiourea species together with the observed shifts of the lead resonance peak from that of a solution containing the same total Pb^{2+} concentration, but no thiourea. The NMR measurements were made at 333K in order to increase solubilities; the equilibrium constants are assumed to apply under these conditions. The mean replacement of water by thiourea reaches only about 0.14 in the most concentrated solution reported upon.

Although fast exchange of the ligands is expected to result in an arithmetic average for the one observed resonance frequency, the change in frequency from pure $Pb(H_2O)_6^{2+}$ to pure $Pb(H_2O)_5tu^{2+}$ (where tu represents the ligand, thiourea) would be expected to be different from that, from pure $Pb(H_2O)_5tu^{2+}$ to $Pb(H_2O)_4tu_2^{2+}$.

As each water is replaced by the ligand thiourea, it might be expected, as a first approximation, that there would be an exponential fall in the Δ Hz value.

From the results in table 3.24 it can be seen that the reported shifts increase relatively slower than the calculated mean replacement figures (0.0303, 0.0637, 0.1002 and 0.1404 for solutions numbered 2-5 respectively).

For solutions numbered 2-4, for which complexes beyond $Pbtu_4^{2+}$ are neglected and for which such complexes are likely to be truly negligible, the results appear to be consistent with a shift of 15.8 KHz for the substitution of one water molecule by thiourea, followed by each subsequent substitution yielding 0.7 of the shift of the previous one. Resonance shifts calculated using this theory are given in the table and are seen to be in reasonable agreement with the experimental values.

The same theory was applied to solution number 5 and was still found to yield quite close agreement. Attempts were made to examine solutions more concentrated in thiourea, but solubility difficulties prevented investigation into regions in which $Pbtu_6^{2+}$ might become significant.

However, an estimate can be made of the resonance frequency for

$Pbtu_6^{2+}$. On the basis of the calculations, the shift of $Pbtu_6^{2+}$ relative to $Pb(H_2O)_6^{2+}$ may be:

$$(15.8 + 15.8 \times 0.7 \times 15.8 \times 0.7^2 + 15.8 \times 0.7^3 + 15.8 \times 0.7^4 + 15.8 \times 0.7^5) \simeq 47 KHz$$

and hence $\frac{Pbtu_6^{2+}}{L}$ would have a frequency of about 18740 KHz.

The NMR shifts of the ^{207}Pb resonance signal for the lead-thiourea systems are probably due to changes in the electronic environment around the lead nucleus. A reasonable assumption would be that, as the thiourea replaces water around the lead nucleus the size of the shift increases a lot by the first addition but not to such a great extent on successive additions, due to saturation type effects in electronic changes.

3.18 Lead with Urea

The results obtained from these experiments indicated that there was little change in the resonance signal when urea was added to the lead nitrate solution. The result would suggest that either no coordination occurred between the lead and urea ligand, or that the coordination obtained gave rise to a ^{207}Pb resonance signal which was very similar to the ^{207}Pb resonance signal obtained for lead nitrate.

Table 3.24

Solution Number	Total $[Pb^{2+}]$	Total [Thiourea]	$[Pb^{2+}]$	[Tu]	$[PbTu_1^{2+}]$	$[PbTu_2^{2+}]$	$[PbTu_3^{2+}]$	$[PbTu_4^{2+}]$	$[PbTu_5^{2+}]$	$[PbTu_6^{2+}]$	Calculated Shifts (KHz)	Actual Shifts (KHz)
1	0.05	-	-	-	-	-	-	-	-	-	0	0
2	0.05	0.0526	0.04183	0.0435	0.00727	0.00087	0.00003	0	0	0	2.77	3.027
3	0.05	0.1051	0.03479	0.08604	0.01197	0.00283	0.00021	0.00020	0	0	5.61	5.432
4	0.05	0.1577	0.02876	0.12765	0.01468	0.00515	0.00057	0.00084	0	0	8.47	8.25
5	0.05	0.2102	0.02361	0.16809	0.01590	0.00734	0.00107	0.00208	0	0	11.38	11.33

Tu = Thiourea

[ ] = Concentration in mol/dm^3

Solution Number – See experimental section Table 3.17 for details of solution content

3.19 Lead with EDTA

The results for ^{207}Pb chemical shift measurements for lead with EDTA are given in tables 3.12, 3.13, 3.14, 3.15. From the data collected, it would seem that adding small quantities of EDTA to a solution of acidic lead nitrate causes the ^{207}Pb resonance signal to occur around the same region as the signal expected for just acidic lead nitrate alone.

If the ratio of the lead salt to EDTA is increased to about 1:1, then the ^{207}Pb resonance signal occurs at a higher frequency than the signal obtained for the same lead concentration in acidic lead nitrate.

Therefore adding EDTA to lead nitrate in molar ratios of 1:1 causes the ^{207}Pb signal to move downfield from the ^{207}Pb signal found for lead nitrate, by up to 2000 ppm.

Using the Jeol FX90Q spectrometer, the maximum observed resonance frequency for these mixtures was 18735.3 KHz. The signal for lead nitrate without added EDTA occurred in the region of 18691 KHz, so it was assumed that any resonance value obtained around 18691 KHz for the mixtures of lead nitrate and EDTA indicated that lead was not complexed to EDTA. Any values obtained near or approaching the 18735.3 KHz value indicated that EDTA was coordinating to the Pb^{2+}. The values in between these indicated that only some EDTA ligand was attached to the lead. It was not certain which part of the EDTA ligand was coordinating to the lead, as the completely deprotonated form of the ligand can complex at four oxygen sites and two nitrogen sites to give six coordination for metals or a five membered chelate ring. Figure 3a shows the structure of EDTA.

The structure of EDTA (ethylene diamine (N, N, N'N'-tetra-acetic acid)

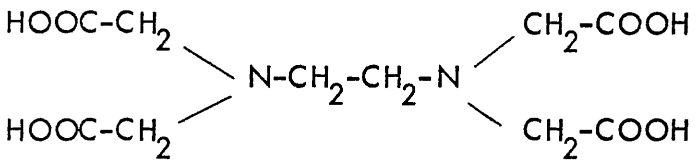


Figure 3a

3.20 Lead Nitrate with EDTA and thiourea

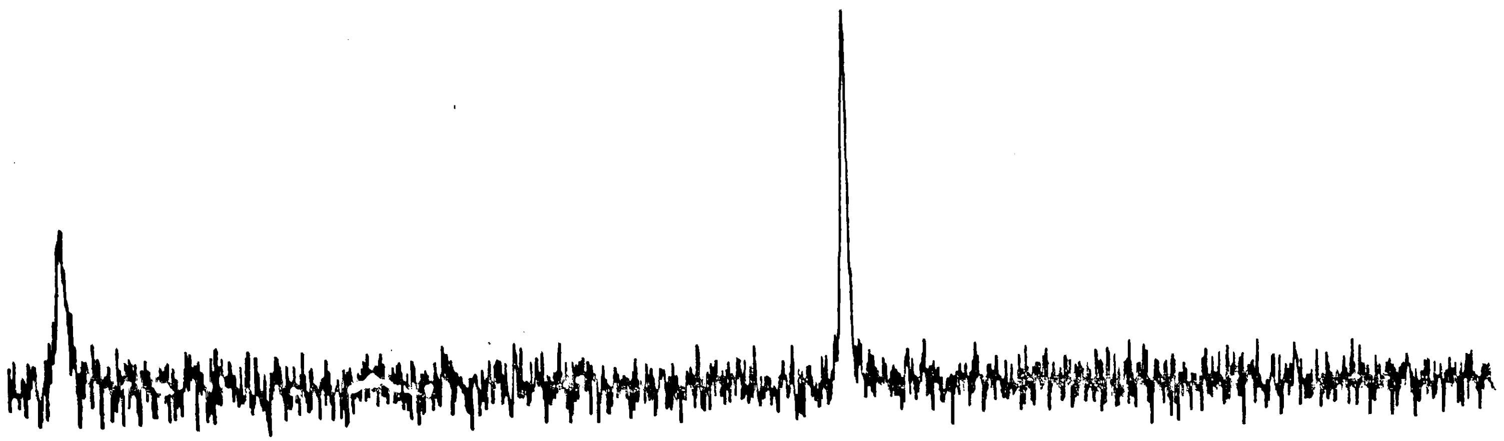
After numerous attempts to combine the two ligands with lead nitrate and maintain an aqueous solution, the following results were obtained (see table 3.16 and Fig. 3b).

A solution was obtained which gave two signals, one signal was probably due to the thiourea ligand, and one signal was probably due to the EDTA ligand. This assumption was made from examining the value of the signal obtained for lead and thiourea mixtures and the value of the signal obtained for lead and EDTA mixtures and comparing these values with the values in table 3.16.

Not all of the solutions could be examined at room temperature as precipitation occurred in some solutions. Raising the solution temperature helped to keep the complexes in solution, but probably would have altered the chemical shift values from the value obtained at lower temperatures, if the experiment had been possible. This factor must be remembered when comparing the data for the mixtures at different temperatures.

The following spectrum (Fig. 3b) shows the ^{207}Pb spectrum of a mixture of lead nitrate with thiourea and EDTA showing the two peaks obtained due to the lead-thiourea and lead-EDTA complexes.

Since the formation constant for PbEDTA is very large, the 'PbEDTA signal' is that produced by the complex, whereas the 'Pb-tu' signal will be the average of $Pbtu_m$ and $Pb(H_2O)_n$.



Spectral width = 25000 Hz

Number of pulses = 40,800

Observation Frequency = 18.72 MHz

OBSET = 10.0 KHz

Temperature = 26°C

Fig. 3b

3.21 Lead nitrate with added citric acid, ascorbic acid and anthranilic acid

The various acids could only be added in very small quantities to the lead nitrate solutions, as large amounts of added ligand caused precipitation of a lead salt.

The ^{207}Pb resonance signal was found to change very slightly with an increase in added ligand in all three cases. Citric acid altered the resonance signal by about 40 ppm (downfield) from the resonance signal of lead nitrate without added ligand at the same temperature and concentration. Ascorbic acid altered the value by 4 ppm (downfield) and anthranilic acid did not appear to have any effect on changing the ^{207}Pb signal from the value of the resonance frequency without added ligand.

3.22 Lead with a variety of ligands

The experimental data given in tables 3.22 and 3.23 show the ^{207}Pb resonance signal changes, when lead is coordinated to different ligands. In Table 3.22 the results were obtained by taking solutions of lead nitrate, lead acetate or lead perchlorate and mixing various ligands with the solutions. The ^{207}Pb resonance frequency results obtained were then compared with the values of the ^{207}Pb resonance frequency obtained for these solutions without added ligand. A significant difference in the values indicated that the lead had undergone a change in coordination. Large changes in resonance frequency were observed with lead nitrate and ethylenediamine, lead nitrate and triethylenetetramine, lead acetate and triethanolamine and lead acetate and sulphamic acid. Unfortunately a range of concentrations of added ligand could not be investigated in each case as only a few ratios of lead salt to ligand produced a mixture which remained in solution and did not precipitate out a lead salt.

Table 3.25 shows the chemical shift differences between the lead salt in solution and the lead bound to a particular ligand in solution.

Table 3.25:

Lead Salt	Ligand	Chemical Shift for Lead Salt (ppm)	Chemical Shift for Lead Ligand Mixture (ppm)	Chemical Shift Difference (ppm)
Lead Nitrate (0.50 mol/dm^3)	Ethylene-diamine (0.50 mol/dm^3)	- 60.1	2859.4	2919.5 (downfield)
Lead Nitrate (0.66 mol/dm^3)	Triethylene-tetramine (0.33 mol/dm^3)	- 68.2	3030.2	3098.4 (downfield)
Lead Acetate (1.00 mol/dm^3)	Sulphamic Acid (Saturated Solution)	1526.1	1406.1	880.1 (upfield)
Lead Acetate (0.50 mol/dm^3)	Triethanolamine (0.50 mol/dm^3)	1490.8	2618.2	1127.4 (downfield)

Table 3.23 shows the results obtained from obtaining solid lead complexes (either purchased or synthesised) and dissolving them in suitable solvents. Many of the compounds studied in this section were found to be soluble in some organic solvents but not water, unfortunately quite a few of the compounds purchased or synthesised were found to be totally insoluble, while others were sparingly soluble in some solvents but not soluble enough to find the ^{207}Pb resonance signal.

All the shifts reported were referenced to the corresponding lead perchlorate value at infinite dilution for consistency with all the other shift data reported in this thesis. Ideally, the compounds should have been referenced to say lead perchlorate in that particular solvent studied, as a solvent change may affect the chemical shift value. Solvent dependency of the chemical shift could not be studied for lead compounds as various lead compounds are only soluble in some solvents, they are not soluble in a range of solvents.

A few of the samples were run completely ^{1}H decoupled. This caused a temperature increase in the sample, but these conditions were necessary to obtain a single sharp ^{207}Pb resonance signal.

CHAPTER FOUR

CADMIUM-113 NMR

4.1 A review of previous ^{113}Cd NMR Studies

The development of F.T. systems has led to an interest in the cadmium nucleus, which has been largely neglected by NMR investigators until recently.[81,82,83,84]

Most papers appear to use as a reference cadmium perchlorate at either 0.1 mol/dm^3 concentration[81,85,86,87] or at infinite dilution.[88,89] The cadmium perchlorate reference cannot be used for INDOR experiments and dimethyl cadmium has been found to be a suitable reference in this case.[90,91] Experiments carried out with dimethyl cadmium have revealed that the signal is very solvent-dependent.[92]

Proctor in 1950 reported the magnetic moment ratio and the resonance frequency ratio of ^{113}Cd and ^{111}Cd.[93] In 1956, Knight shift measurements were carried out on the isotopes. From 1950 to 1970 there have been several reports of cadmium resonances in metals and alloys.[94,95]

Reports of INDOR studies have been rather sparse, although Hildenbrand and Dreeskamp have carried out some studies in this area.[96] Suitable satellites to study INDOR techniques for a lot of cadmium complexes are unavailable due to the lability of cadmium complexes so the present data have been limited to organometallic cadmium derivatives.[90,91] Signal broadening has been observed in ^{113}Cd enriched samples[97].

A value of the absolute resonance frequency, (Ξ), for ^{113}Cd has been reported by Kennedy and McFarlane,[91] but the reliability of the value is not known.

Methyl cadmium alkoxides are believed to be tetrameric[91] and some of the complexes show two NMR signals, after a day in solution. The authors have said that this is due to the presence of hexamers. Two signals have been observed in a few other solutions, for instance, cadmium with bovine carbonic anhydrase[97] and for cadmium in the complex $Cd_{10}(SCH_2CH_2OH)$.[87] It is thought that many solutions contain several species, but usually only one NMR signal for the ^{113}Cd nucleus is observed due to the lability of cadmium complexes, especially in aqueous solution. It has been suggested that it may be impossible to compare say cadmium nitrate with say a cadmium glycine complex under the same conditions, but Kostelnik and Bothner-by have attempted to link some results by adding small amounts of a series of ligands to aqueous solutions of cadmium sulphate. The results do show a trend and the authors have concluded that ligands coordinated through oxygen give shifts to lower frequency, while ligands coordinated through nitrogen and sulphur give shifts to higher frequency.[98]

^{113}Cd resonances have been observed for some perchlorate, sulphate and nitrate solutions.[88,89] Krüger et al have published a value for shielding for $Cd(H_2O)_6^{2+}$ as being -1106(4) ppm from the free atom.[89]

^{113}Cd signals for cadmium perchlorate, sulphate and nitrate have been briefly surveyed and they have been found to extrapolate to the same point at low concentrations.[89,88]

Results for cadmium halides[99,100] have been obtained and show a non-linear concentration dependence due to the association constants involved.[88]

A number of papers have been published on cadmium resonances linked with biochemical systems.[101,113]

A recent ^{113}Cd NMR study has been carried out by Jensen and Deshmukh on cadmium-EDTA complexes.[114]

4.2 Coupling Constants

Cadmium-proton coupling has been reported in dialkyl cadmiums[96,90] and cadmium alkoxides.[90] Cadmium-phosphorus couplings have been found for alkyl and alkyl-aryl phosphine cadmium compounds.[115,116]

4.3 Results for ^{113}Cd Chemical Shift Measurements

Table 4.1: Cadmium Nitrate in Acidic Solution

This experiment was carried out to investigate the effect of temperature and concentration on ^{113}Cd resonance signal in samples of acidic cadmium nitrate at pH 0.91.

Temperature (K)	Concentration of Cadmium Nitrate mol/dm^3	Resonance Frequency (KHz)	Chemical Shift (ppm)
288	1.00	19872.900	-22.6
288	0.50	19873.080	-13.6
288	0.25	19873.165	- 9.3
288	0.10	19873.210	- 7.0
288	0.05	19873.240	- 5.5
299	1.00	19872.870	-19.4
299	0.50	19873.020	-11.8
299	0.25	19873.110	- 7.3
299	0.10	19873.170	- 4.3
299	0.05	19873.170	- 4.3
313	1.00	19872.760	-23.4
313	0.50	19872.950	-13.8
313	0.25	19873.040	- 9.3
313	0.10	19878.115	- 5.5
313	0.05	19873.120	- 5.3

GRAPH 4.1

GRAPH OF RESONANCE FREQUENCY CHANGING WITH CONCENTRATION AND TEMPERATURE FOR A SERIES OF ACIDIC CADMIUM NITRATE SOLUTIONS

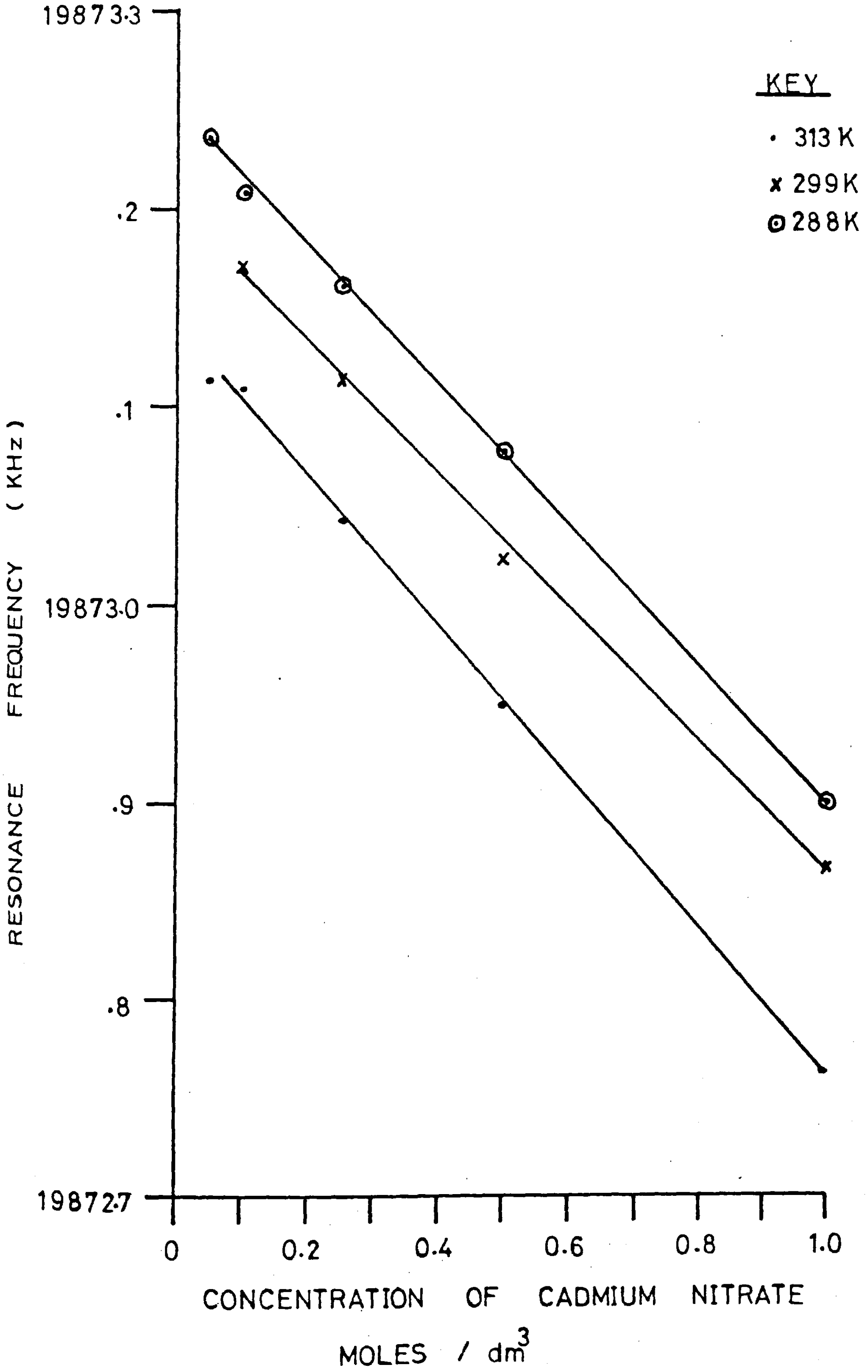


Table 4.2: Cadmium Sulphate in Acid Solution

The following results show the change in resonance frequency for ^{113}Cd for a series of acidic cadmium sulphate solutions at various temperatures and concentrations.

Temperature (K)	Concentration of Cadmium Sulphate mol/dm^3	Resonance Frequency (KHz)	Chemical Shift (ppm)
288	0.50	19873.240	- 4.38
288	0.25	19873.265	- 2.31
288	0.10	19873.285	- 2.0
288	0.05	19873.290	- 1.8
299	0.50	19873.175	- 3.8
299	0.25	19873.190	- 3.0
299	0.10	19873.205	- 2.3
299	0.05	19873.210	- 2.0
313	0.50	19873.095	- 6.5
313	0.25	19873.125	- 5.0
313	0.10	19873.150	- 3.8
313	0.05	19873.155	- 3.5

GRAPH 4.2

GRAPH OF RESONANCE FREQUENCY CHANGING WITH CONCENTRATION AND TEMPERATURE FOR A SERIES OF ACIDIC CADMIUM SULPHATE SOLUTIONS

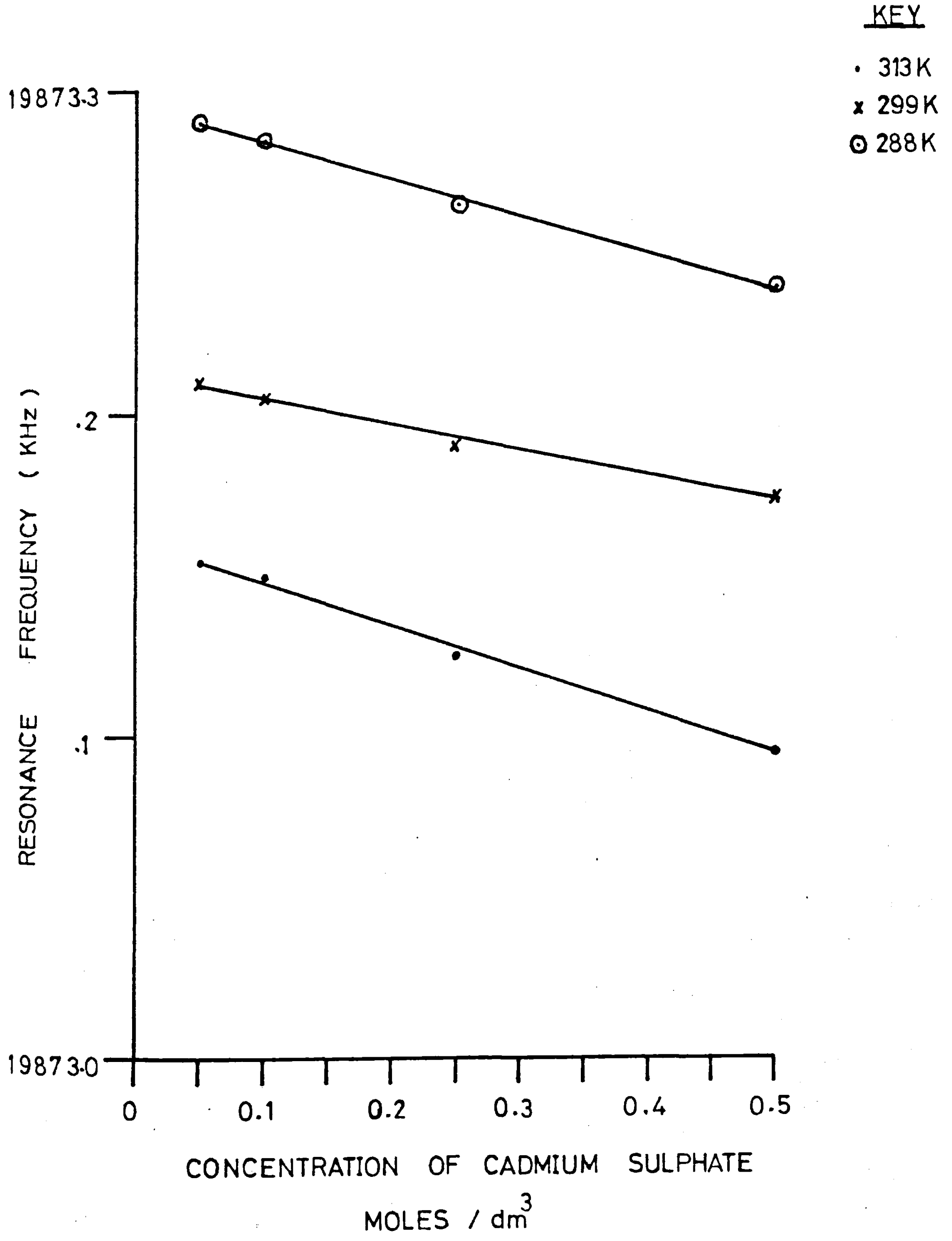


Table 4.3: Cadmium Acetate in Acid Solution

Table 4.3 shows the data collected for acidic solutions of cadmium acetate at various concentrations and temperatures.

Temperature (K)	Concentration of Cadmium Acetate mol/dm^3	Resonance Frequency (KHz)	Chemical Shift (ppm)
288	1.00	19872.600	-36.5
288	0.50	19872.700	-31.5
288	0.25	19872.785	-27.2
288	0.10	19872.880	-22.4
288	0.05	19872.975	-17.6
299	1.00	19872.585	-33.5
299	0.50	19872.665	-29.4
299	0.25	19872.730	-26.2
299	0.10	19872.840	-20.6
299	0.05	19872.920	-16.6
313	1.00	19872.565	-33.2
313	0.50	19872.630	-29.9
313	0.25	19872.690	-26.9
313	0.10	19872.780	-22.4
313	0.05	19872.850	-13.8

GRAPH 4.3

GRAPH OF RESONANCE FREQUENCY CHANGING WITH CONCENTRATION AND TEMPERATURE FOR A SERIES OF ACIDIC CADMIUM ACETATE SOLUTIONS

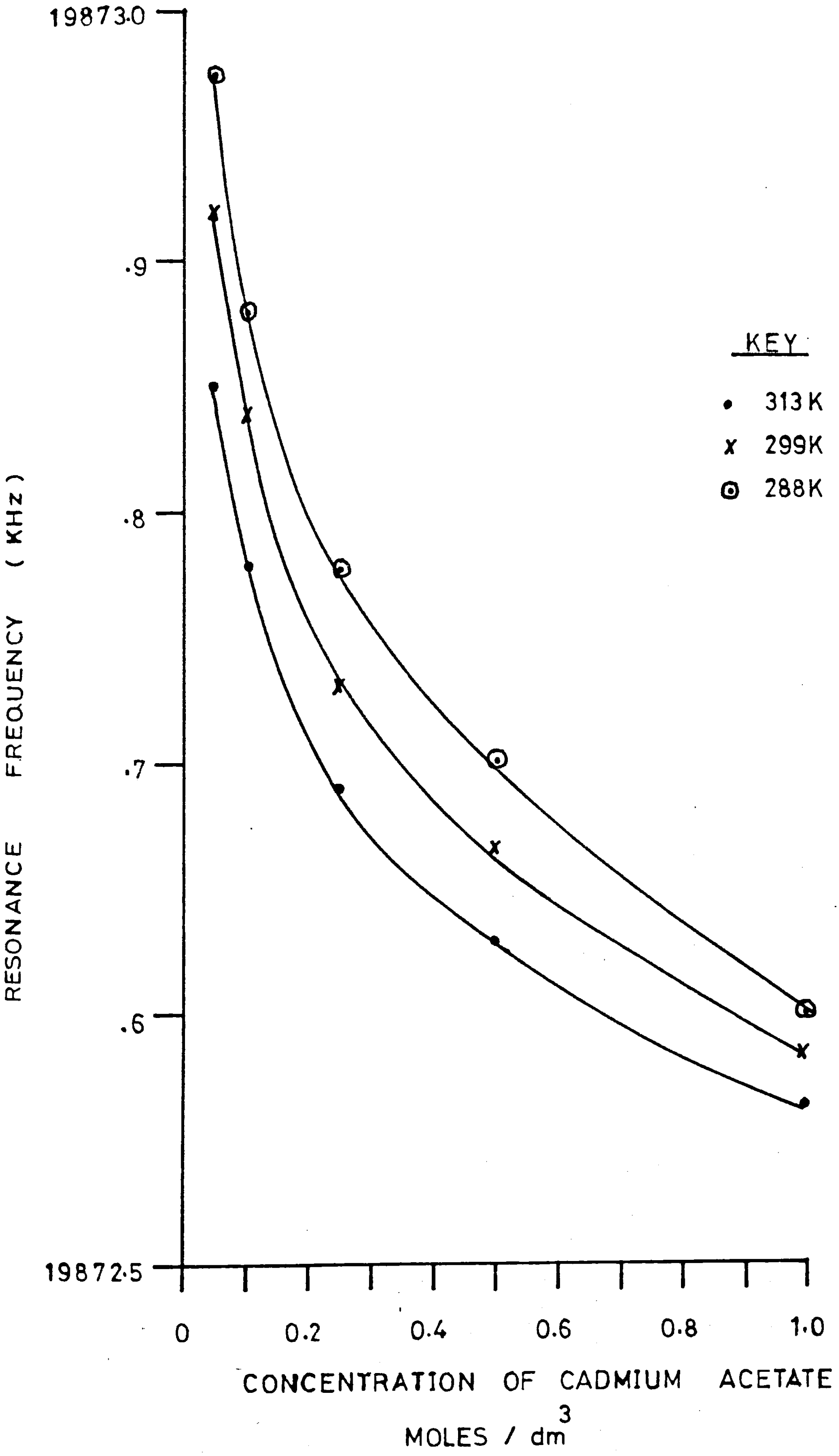


Table 4.4: Cadmium Iodide in Acid Solution

Temperature (K)	Concentration of Cadmium Iodide (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
288	1.00	19874.390	53.6
288	0.50	19874.450	56.6
288	0.25	19874.470	57.6
288	0.10	19874.435	55.9
288	0.05	19874.340	51.1
299	1.00	19874.375	56.6
299	0.50	19874.445	60.1
299	0.25	19874.440	59.9
299	0.10	19874.375	56.6
299	0.05	19874.250	50.3
313	1.00	19874.360	57.1
313	0.50	19874.410	59.6
313	0.25	19874.405	59.4
313	0.10	19874.335	55.9
313	0.05	19874.215	49.8

GRAPH 4.4

GRAPH OF RESONANCE FREQUENCY CHANGING WITH CONCENTRATION AND TEMPERATURE FOR A SERIES OF ACIDIC CADMIUM IODIDE SOLUTIONS.

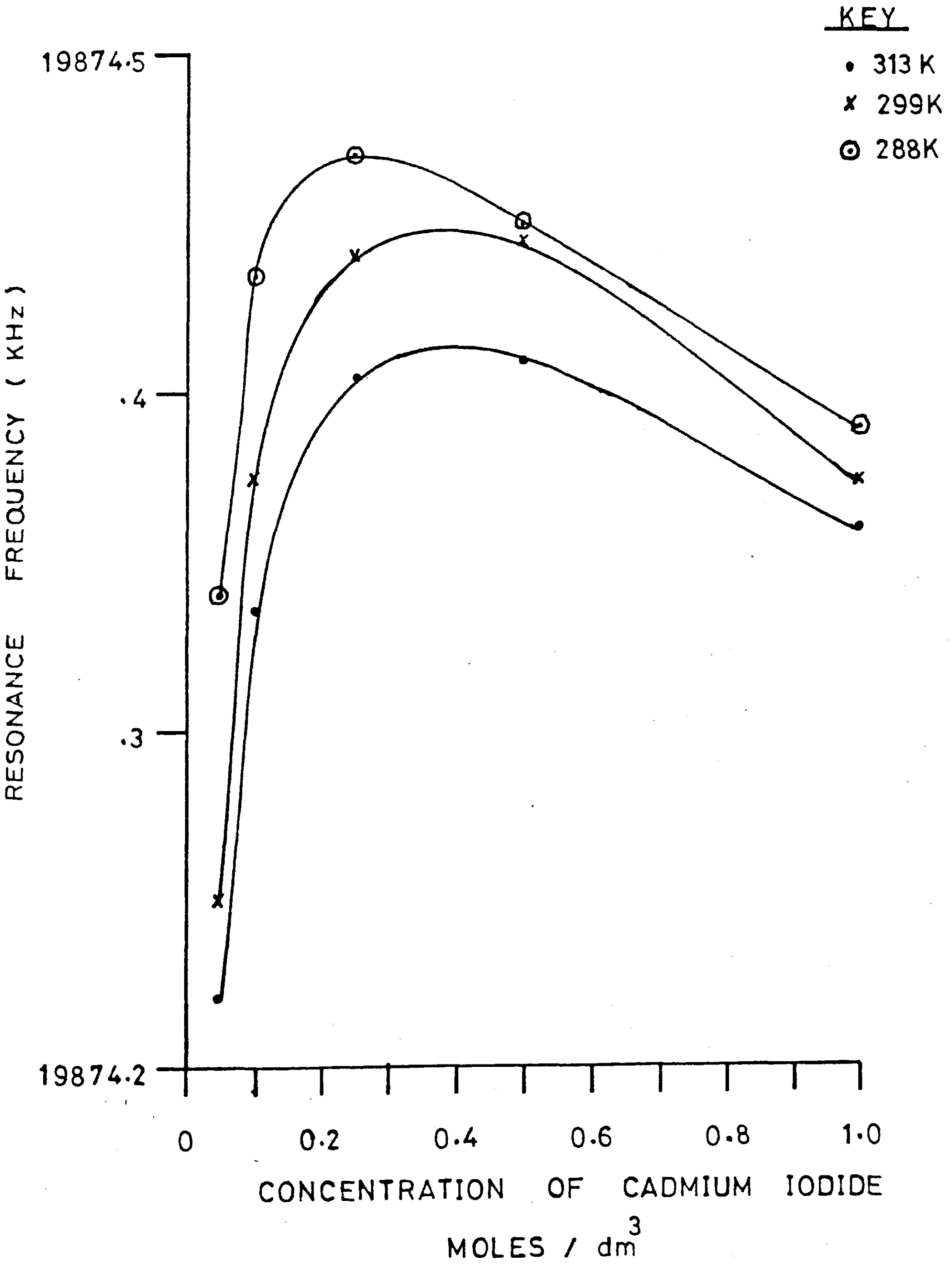


Table 4.5: Cadmium Chloride in Acid Solution

Temperature (K)	Concentration Cadmium Chloride (mol/dm^3)	Resonance Frequency (KHz)	Chemical Shift (ppm)
288	1.00	19875.265	97.6
288	0.50	19874.995	84.0
288	0.25	19874.765	72.5
288	0.10	19874.525	60.4
288	0.05	19874.410	54.6
299	1.00	19874.275	101.9
299	0.50	19875.020	89.1
299	0.25	19874.765	76.2
299	0.10	19874.525	64.2
299	0.05	19874.405	58.1
313	1.00	19875.310	104.9
313	0.50	19875.045	91.6
313	0.25	19874.780	78.2
313	0.10	19874.530	65.7
313	0.05	19874.410	59.6

GRAPH 4.5

GRAPH OF RESONANCE FREQUENCY CHANGING WITH CONCENTRATION AND TEMPERATURE FOR A SERIES OF ACIDIC CADMIUM CHLORIDE SOLUTIONS

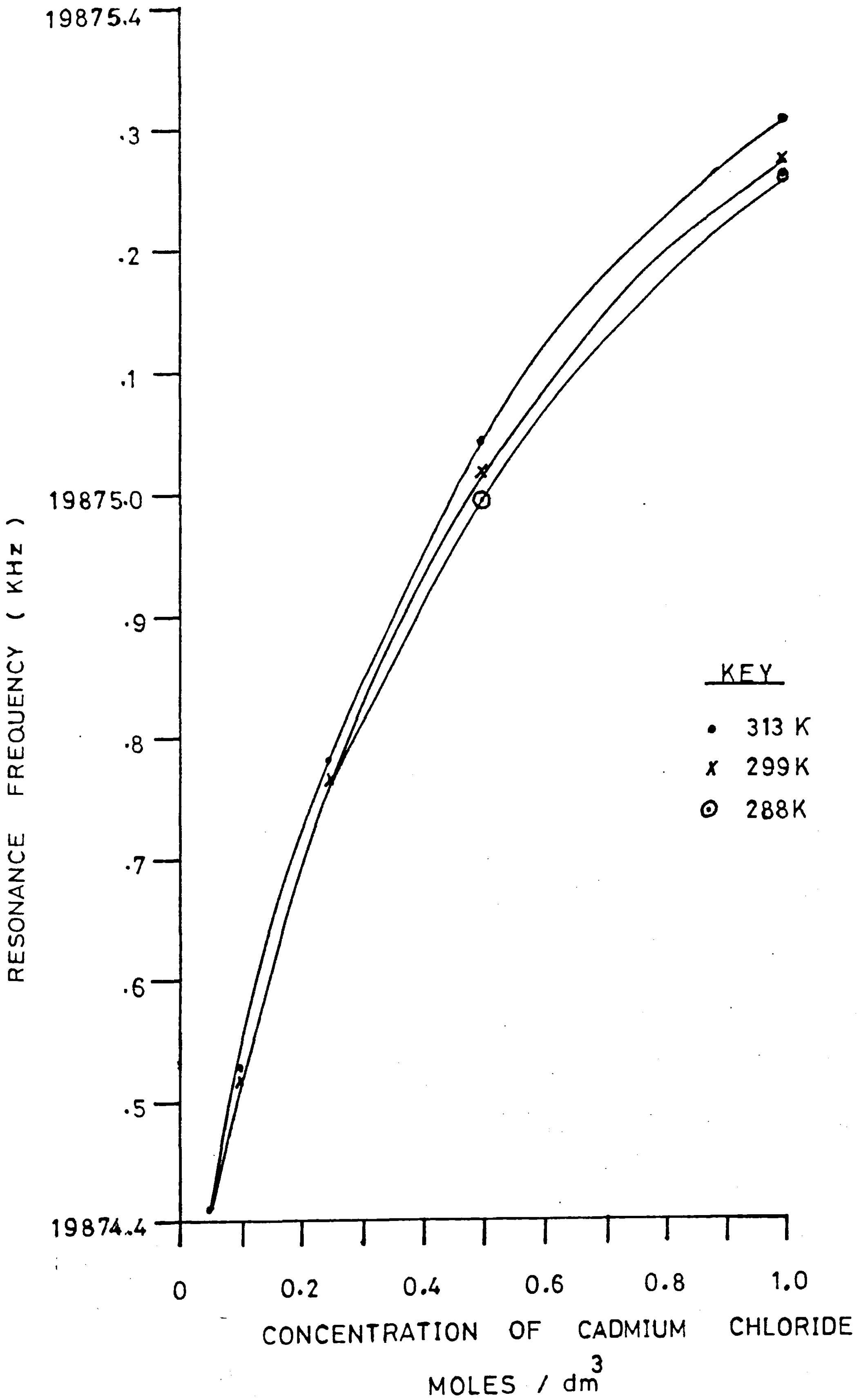


Table 4.6: Cadmium Perchlorate in Acid Solution

Temperature (K)	Concentration of Cadmium Perchlorate mol/dm^3	Resonance Frequency (KHz)	Chemical Shift (ppm)
288	1.00	19873.275	- 2.5
288	0.50	19873.285	- 2.0
288	0.25	19873.295	- 1.5
288	0.10	19873.310	- 0.5
288	0.05	19873.315	- 0.52
288	Infinite Dilution	19873.325	0.01
299	1.00	19873.200	- 2.5
299	0.50	19873.220	- 1.51
299	0.25	19873.225	- 1.3
299	0.10	19873.230	- 1.0
299	0.05	19873.245	- 0.3
299	Infinite Dilution	19873.250	0.0
313	1.00	19873.160	- 3.3
313	0.50	19873.185	- 2.0
313	0.25	19873.195	- 1.5
313	0.10	19873.200	- 1.36
313	0.05	19873.210	- 0.8
313	Infinite Dilution	19873.225	0.0

GRAPH 4.6

GRAPH OF RESONANCE FREQUENCY CHANGING WITH CONCENTRATION AND TEMPERATURE FOR A SERIES OF ACIDIC CADMIUM PERCHLORATE SOLUTIONS

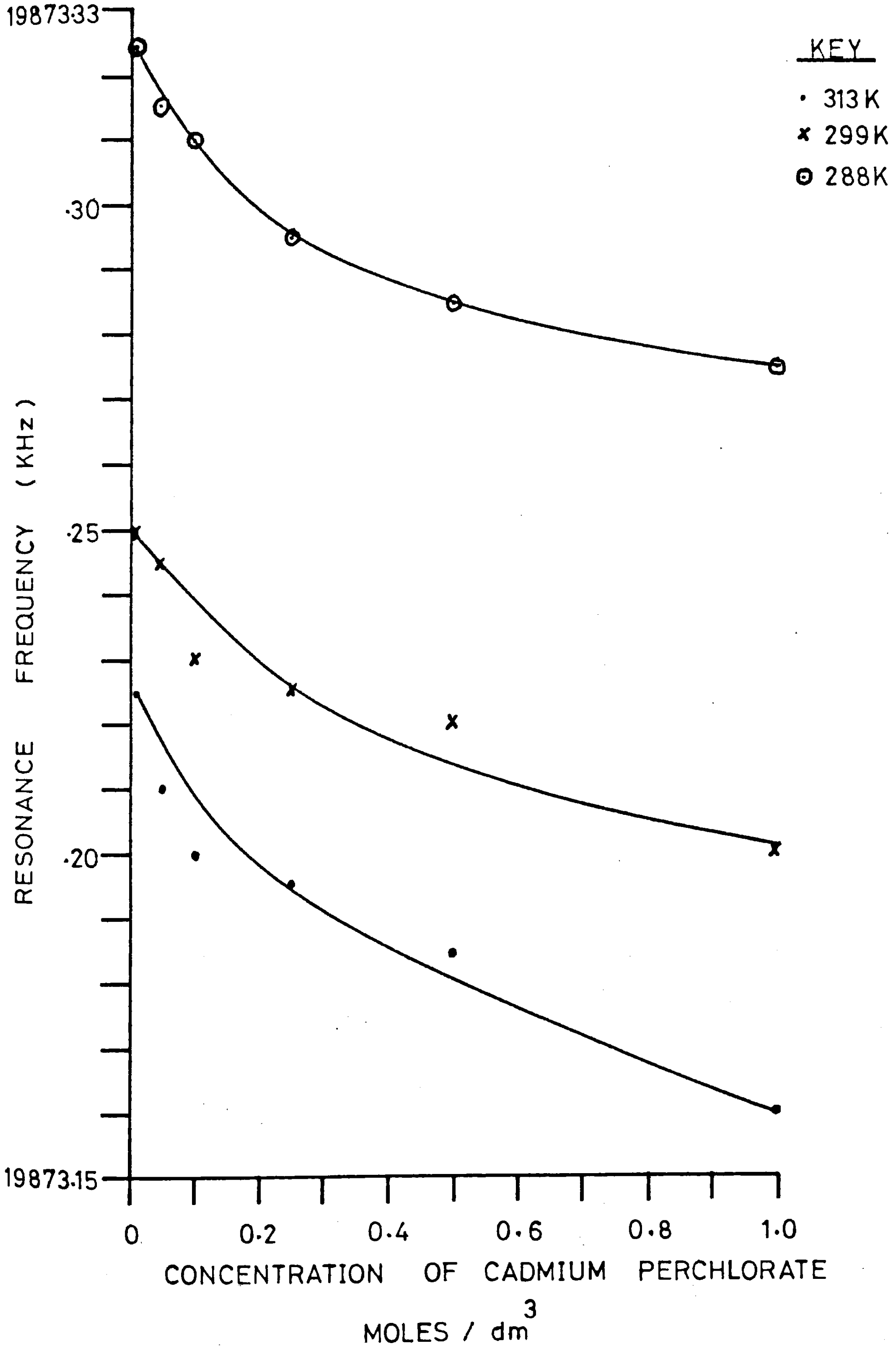


Table 4.7: Cadmium Nitrate in an Acid Solution of Methanol and Water (V:V 50:50) at pH 0.90

Temperature (K)	Concentration Cadmium Nitrate mol/dm^3	Resonance Frequency (KHz)	Chemical Shift (ppm)
299	1.00	19872.795	-22.9
299	0.50	19872.960	-14.6
299	0.25	19873.055	- 9.8
299	0.10	19873.120	- 6.5
299	0.05	19873.150	- 5.0
313	1.00	19872.505	-36.2
313	0.50	19872.795	-21.6
313	0.25	19872.825	-20.1
313	0.10	19872.900	-16.3
313	0.05	19872.950	-13.8

Table 4.8: Cadmium Fluoride in Aqueous Solution

Solutions of cadmium fluoride in acid solution were made but a white precipitate formed on each occasion, so very dilute solutions of cadmium fluoride without acid were made up and precipitation did not occur.

Concentration of Cadmium Fluoride mol/dm^3	Resonance Frequency (KHz)	Chemical Shift (ppm)	Linewidth (Hz)
0.075	19873.200	-2.5	5
0.05	19873.215	-1.8	5
0.025	19873.225	-1.3	5

Table 4.9: ^{113}Cd Resonance Signal in some Cadmium Complexes

Cadmium Complex	Solvent and Concentration	Resonance Frequency (KHz)	Chemical Shift (ppm)
Bis (ethyl-L-cysteineate) Cadmium II	Acidic Solution Saturated	19876.560	166.6
Cadmium Nitrate with Triethylene-tetramine	Water/ Triethylene-tetramine	19878.526	265.5

4.4 Experimental

The experiment chemical shift data for ^{113}Cd were obtained using similar methods to the way in which the lead chemical shift data were obtained (Chapter 3, section 3.2).

Preparations

1. Bis (ethyl L-cysteineato) cadmium II[78]

Ethyl L-cysteineate hydrochloride (0.015 mole) was dissolved in water (10 ml) and cooled to 0°C. An ice-cold solution of sodium hydroxide (0.03 mole) in water (10 ml) was added to the solution and then a solution of cadmium nitrate (0.005 mole) in water (15 ml) was added dropwise with continuous stirring. A white precipitate separated, which dissolved on stirring. The solution was then allowed to stand for about 15 minutes and colourless crystals began to precipitate. The crystals were collected and washed with alcohol and water.

2. Tetrakis (L-cysteineato) tricadmium (II) tetrachlorocadmate (II)[117]

L-cysteine (0.04 mole) was dissolved in warm water (100 ml). A solution of warm cadmium chloride (0.04 mole) in a small volume of water was added with stirring and a white precipitate formed. The solution was stirred for ca 2 hours and then the precipitate was filtered, washed first with water then with absolute ethanol and dried in vacuo over calcium chloride.

4.5 Cadmium nitrate in acid solution

The chemical shift data of these solutions indicated that the resonance frequency of the ^{113}Cd signal decreased in frequency with increasing cadmium concentration. This was similar to the lead nitrate result and decreased with increasing temperature, which was found to be the opposite to the lead nitrate trend.

The results have been tabulated in table 4.1 and shown graphically in graph 4.1.

4.6 Cadmium sulphate in acid solution

The ^{113}Cd signal was found to decrease, slightly, with increasing concentration of the cadmium salt. The graph plot of resonance frequency vs concentration (graph 4.2) gives an almost linear plot which indicates a small association constant.[88]

The ^{113}Cd resonance signal decreases in resonance frequency with increasing temperature at a particular concentration.

4.7 Cadmium acetate in acid solution

The ^{113}Cd resonance signal decreases in resonance frequency with increasing concentration and temperature. Lead acetate did not show similar behaviour.

4.8 Cadmium perchlorate in acid solution

These results show an almost linear plot with changing resonance frequency and concentration (graph 4.6). The signal moved to higher field with increasing concentration. The ^{113}Cd resonance signal was found to decrease in frequency with increasing temperature.

4.9 Cadmium nitrate in acid solution with methanol and water

This experiment was carried out to investigate any change in resonance signal with changing solvent. The ^{113}Cd resonance signal was found to increase in frequency by adding methanol, by about 10 ppm.

The association between cadmium and counter ion should be increased by substituting a nonliganding solvent for water.[119] The observed shift in this case is to lower field.

4.10 Cadmium halides in acid solution

The halides studied were: cadmium iodide, cadmium chloride and cadmium fluoride.

Cadmium fluoride was found to be only slightly soluble in aqueous solution without acid, so only dilute solutions could be studied (0.075 mol/dm^3). The results are given in table 4.8.

Cadmium chloride and cadmium iodide were studied in acidic solution. Both sets of data show a non-linear dependence of resonance frequency on concentration (graph 4.5 and graph 4.4). In the case of cadmium iodide the resonance frequency of the ^{113}Cd signal increases with increasing concentration, i.e. moves to lower field, and then decreases with increasing concentration, i.e. moves to higher field. In the case of cadmium chloride, the resonance frequency of the ^{113}Cd signal increased with increasing concentration.

The very different nature of the plots for the iodide and chloride may be due to higher order halide complexes existing in solution.

CHAPTER FIVE

ION-PAIRING

5.1 Ions in Solution[120]

When any metal salt is placed in aqueous solution, there are several equilibria that could be competing in the solution. The suggested reactions are; hydrolysis, ion pairing, polymerisation and cluster formation.

Hydrolysis is a term applied to chemical reactions where a substance is decomposed or split by water. In inorganic chemistry the term hydrolysis has been applied to solutions of salts and the reactions by which they are converted to new ionic species or to precipitates, such as; basic salts, oxides or hydroxides.

Aquo cations, especially in +2, +3 and +4 oxidation states are normally acidic in solution. A simple approach is to consider the cations transferring a proton to the solvent in the following way:

$$H_2O + \left[M(H_2O)x\right]^{n+} \longrightarrow \left[M(H_2O)_{x-1}\ (OH)\right]^{(n-1)^+} + H_3^+O$$

Most metal atoms of the form M^{n+} form strong bonds to oxygen and hydroxide ligands. Oxygen and hydroxide ligands are always present in water at concentrations over quite a wide range i.e. $> 1 < 10^{-14}$M, due to the small self-dissociation constant (Kw) of water.

$$Kw = [H^+][OH^-] \simeq 10^{-14}\ M^2$$

Owing to the large range of hydroxide complexes which may be formed in solution, the resulting chemical behaviour of a given metal in a given valence may be a complicated function of pH and concentration.

Ion pairing in solution results from electrostatic interactions between ions of opposite charge. This causes ions to group together and move more slowly under the influence of an electric field. In NMR experiments, it has been suggested that ion-pairing is thought to be responsible for chemical shift measurements changing with concentration in a non-linear fashion. The effects of ion pairing may be decreased, in some cases, by adding strong complexing agents to the solutions, which remove anions from around the cations.

There are two (possibly limiting) types of ion pairs, tight (contact) ion pairs and loose (solvent separated) ion pairs. The contact ion pairs have short interionic distances, with no intervening solvent molecules between the charged sites, so chemical shifts are sensitive to the counter ion. The solvent separated ion pairs have longer interionic distances than the contact ion pairs, due to the presence of one or more solvent molecules between the charged sites. The chemical shifts due to this type of ion pairing are independent of the counter ion and dominated by solvent effects.

Polymerisation in solution occurs when complexes in solution form with more than one metal ion. An example of this can be found with some metal and hydroxide ions.

Cluster formation may also be another process occurring in solution. This occurs when bridges form between the ligands and metal ions and form overall three dimensional structures in solution.

5.2 The nature of lead in solution

Naturally occurring lead exists in three oxidation states, O, +2, +4[121]. The +2 state is the most common state, with the electronic configuration (Xe) $4f^{14}\ 5d^{10}\ 6s^{2}$, it is also the state with the most complex hydrolysis behaviour.[122] The +2 state is more stable than the +4 state, due to the $6s^2$ electrons in the divalent state giving rise to a phenomenon known as the inert pair effect. This effect reduces the extent of back bonding between the metal and the ligand, which suggests that lead in the +2 oxidation state would form the most stable complexes with highly polarisable ligands. Lead does not form $p\pi$ bonds under any circumstances.

Aqueous solutions of lead are stable only below pH 5. Complex formation between lead in the +2 oxidation state and hydroxide ions has been studied in perchlorate solutions. The following species are thought to be present in the solution before precipitation occurs:

$Pb(OH)_3^-$ $Pb_4(OH)_4^{4+}$ Pb_2OH^{+3} $Pb(OH)_2$

$Pb(OH)_4^{+2}$ $PbOH^+$ $Pb_6(OH)_8^{4+}$

$Pb_4(OH)_4^{4+}$ is thought to be the predominant species.[123] All these species will of course be further interacting with water molecules.

5.3 The nature of cadmium in solution

Cadmium exists in the +2 oxidation state in aqueous solution. The aqueous ions of cadmium are quite strong acids and are hydrolysed. The Cd^{2+} ion forms quite stable aqueous complexes with ammonia, cyanide, halide and hydroxide ions.

Hydrolysis of Cd^{2+} becomes significant above pH 7 in concentrated solutions. Polynuclear species are formed in small amounts and then cadmium hydroxide begins to precipitate. Above pH 8 mononuclear hydrolysis products are formed, but they are difficult to observe as dissolved entities as they precipitate even at low concentrations. Above pH 13 the solubility of the hydroxides increases due to the formation of $Cd(OH)_4^{2-}$

Generally, cadmium salts are more soluble in water than the corresponding lead salts and there are more water soluble cadmium salts than there are water soluble lead salts.

The range of chemical shift has been found to be smaller for ^{113}Cd than for ^{207}Pb (see chapters 3 and 4).

The linewidths found for the ^{113}Cd resonance signal in various cadmium salts do not appear to be altered greatly by changing the temperature of the sample. This indicates fast exchange. The corresponding ^{207}Pb signal does show a change with temperature.

Forsén and coworkers[124] have recently demonstrated the great potential of cadmium NMR studies to ion-binding phenomena.

5.4 The calculation of equilibrium constants from NMR data

The model used to obtain the equilibrium constants from the ^{207}Pb and ^{113}Cd NMR data was based on a modified version of the Debye-Huckel theory. The calculations were carried out with the aid of a computer program which involved calculating activity coefficients for a series of solutions, varying in concentration for salts of lead or cadmium at specified temperatures by comparing the salt under investigation with a perchlorate solution at that concentration. The concentration range was varied from 0.001 mol/dm^3 to 2.000 mol/dm^3.

The model used involved several assumptions, firstly, that magnetically x mol/dm^3 of lead nitrate would give the same susceptibility effect as x mol/dm^3 of lead perchlorate; secondly, that the lead perchlorate solutions were not ion paired significantly at the concentrations investigated, and thirdly, if two species are present exchanging the resonating nucleus, the signal is recorded at the arithmetic mean position of the two pure species' resonances if the exchange is rapid.

All theoretical forms of calculating activity coefficients of ions are based on the Debye-Huckel theory. The basic equation giving reasonable approximations to the theoretical results for a binary electrolyte may be represented as:

[125]

$$-\log {}_{\pm} f = \frac{A z_+ z_- \sqrt{I}}{1 + Ba\sqrt{I}}$$

where z_+z_- = the positive values of the product of the charges on the ions

A = a temperature dependent constant which may be given as:

$$A = 1.825 \times 10^{6} \quad (\varepsilon T)^{-3/2}$$

where ε = dielectric constant

T = temperature

I = ionic strength, which may be given as:

$$I = \tfrac{1}{2} \sum C_i Z_i^2$$

where C = concentration

i = particular ion

B = constant, which may be given as:

$$B = 50.3 \quad (\varepsilon T)^{\frac{1}{2}}$$

a = an adjustable parameter which represents the effective size of the hydrated ion.

N.B. recent data gives ε in water at 25°C as 78.30

A in water at 25°C as 0.5115

This basic equation is sometimes modified to regard the product Ba as unity, but more particularly Huckel and Gugenheim[126] introduced an additional linear term $-CI$ which was originally supposed to allow for variations in the dielectric constant caused by the presence of the solute. Now C is taken more empirically as yet another adjustable parameter.

Davies[127] has produced arguments for the empirical use of a constant value of C, but if C is allowed to be adjustable, better results seem to be obtained.

A term with the overall negative sign as indicated by $-CI$ is required to account for the common fact that experimentally different activity coefficients pass through a minimum often in the region of 0.5-1.0 mol/dm^3 solute.

The above equations were the basis of the calculations used to obtain the equilibrium constant data.

The equilibrium constant data were collected by measuring the resonance frequency of various concentrations of the particular salt under investigation, and then comparing these values with values of resonance frequency measurements taken for the perchlorate salt under corresponding conditions. The differences in the resonance frequency values, Δ Hz, were then used in the calculations. These values for lead nitrate are shown in Table 5.1.

The calculations were carried out using the VAX 11/780 computer at Bedford College, London.

5.5 Lead Nitrate Data

The following results (Table 5.2) show the data obtained for the equilibrium constant for acidic solutions of lead nitrate at various temperatures.

The single ^{207}Pb resonance signal for each solution of lead nitrate, has been taken to be due to the rapid exchange between Pb^{2+} (aqueous) and $PbNO_3^+$ (aqueous). In the lead perchlorate case, it has been assumed that only one species is present, that is Pb^{2+} (aqueous).

Lead perchlorate in acid solution does show a change in resonance frequency with concentration (graph3.1). This is probably due to effects such as the changes in bulk susceptibility due to ionic concentration.

For the calculations, it has been assumed that the above mentioned effect and any other effects are the same in both the perchlorate and nitrate cases and $Pb(ClO_4)_2$ is not ion-paired significantly at the concentrations investigated. The lead tetrafluoroborate and lead dithionate results seem to support this assumption.

If only one ion-paired species is present in the lead nitrate case, then the Δ Hz values should be directly proportional to:

$$\frac{[PbNO_3^+]}{[Pb^{2+}] + [PbNO_3^+]}$$

In these ionic solutions, the equilibrium constant for the reaction:

$$Pb^{2+} + NO_3^- \rightleftharpoons PbNO_3^+$$

varies with ionic strength (I).

It was then assumed that the activity coefficients (f) varied with I in the following way:

$$-\log f_i = 0.5\, z_i^2 \left(\frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} - C\ I \right) \text{ at } 298\text{K}$$

and K_O is related to K_C by:

$$K_O = K_C \frac{f_1}{f_1 f_2} = \frac{K_C}{f_2}$$ where: 1 and 2 refer to the ionic charge

For lead nitrate:

$$\frac{[\text{PbNO}_3^{+}]}{[\text{Pb}^{2+}][\text{NO}_3^{-}]} = K_C$$

$$[\text{PbNO}_3^{+}] = [\text{Pb}^{2+}][\text{NO}_3^{-}]\ K_0 f_2$$

and since

$$\Delta\ \text{Hz} \propto \frac{[\text{PbNO}_3^{+}]}{[\text{Pb}^{2+}][\text{NO}_3^{-}]}$$

the following equation may be written:

$$\frac{\Delta\ \text{Hz}}{B} = \frac{K_0[\text{NO}_3^{-}]\ \log_{10}^{-1}\left\{ -A\ \dfrac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} + C I \right\}}{1 + K_0[\text{NO}_3^{-}]\ \log_{10}^{-1}\left\{ -A\ \dfrac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} + C I \right\}}$$

where: B = proportionality constant

C = constant

A = temperature dependent constant

From the results, it has been predicted that at zero concentration if $PbNO_3^+$ were present alone under these conditions, the resonance frequency would be 18683.600 KHz.

The value of K obtained at 299K is in quite good agreement with the value found in the literature[128] (3.162) for lead nitrate under these conditions found using another technique to calculate K.

Graph 5.2 shows the Arrhenius plot for these data. The slope and the intercept of the graph were found using a least squares fit program on a BBC microcomputer. The plot was carried out to find $\Delta H^\ominus$ and $\Delta S^\ominus$ for lead nitrate by using the following equations:

$$\Delta G^\ominus = -RT \ln K$$

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

$$-RT \ln K = \Delta H^\ominus - T\Delta S^\ominus$$

$$-R \ln K = \frac{\Delta H^\ominus}{T} - \Delta S^\ominus$$

$$\ln K = -\frac{\Delta H^\ominus}{RT} + \frac{\Delta S^\ominus}{R}$$

A plot for a straight line graph is given by:

$$y = mx + c$$

A graph plot of:

$\ln K$ vs $\frac{1}{T}$ gives: intercept $= \frac{\Delta S^\ominus}{R}$

slope $= -\frac{\Delta H^\ominus}{R}$

If R = gas constant = 8.314 for $PbNO_3^+$ formation

slope = -1105 $\Delta H^\ominus = 9.2 \text{ kJ mol}^{-1}$

Intercept = 4.96 $\Delta S^\ominus = 41 \text{ JK}^{-1} \text{ mol}^{-1}$

Table 5.1: Data used for calculating K values for acidic lead nitrate solutions

Temperature (K)	Concentration of Lead Nitrate (mol/dm^3)	^{207}Pb Resonance Frequency for Lead Nitrate (KHz)	^{207}Pb Resonance Frequency for Lead Perchlorate under corresponding Conditions (KHz)	Difference in Resonance Frequencies Δ Hz (KHz)
278	1.00	18689.570	18692.600	3.030
278	0.85	18689.630	18692.485	2.855
278	0.65	18689.800	18692.325	2.525
278	0.50	18689.950	18692.190	2.240
278	0.40	18690.045	18692.800	2.755
278	0.30	18690.220	18691.970	1.750
278	0.25	18690.320	18691.930	1.610
278	0.20	18690.380	18691.860	1.480
278	0.10	18690.660	18691.740	1.080
278	0.05	18690.830	18691.670	0.840
288	1.00	18689.940	18692.645	2.705
288	0.85	18690.053	18692.530	2.477
288	0.65	18690.110	18692.375	2.265
288	0.50	18690.264	18692.245	1.981
288	0.40	18690.370	18692.150	1.780
288	0.30	18690.517	18692.040	1.523
288	0.25	18690.695	18691.975	1.280
288	0.20	18690.700	18691.935	1.240
288	0.10	18690.910	18691.825	0.915
288	0.05	18691.075	18691.770	0.695

Table 5.1 (continued)

Temperature (K)	Concentration of Lead Nitrate (mol/dm^3)	^{207}Pb Resonance Frequency for Lead Nitrate (KHz)	^{207}Pb Resonance Frequency for Lead Perchlorate under corresponding Conditions (KHz)	Difference in Resonance Frequencies Δ Hz (KHz)
299	1.00	18690.158	18692.645	2.487
299	0.85	18690.258	18692.550	2.292
299	0.65	18690.145	18692.420	2.005
299	0.50	18690.566	18692.315	1.749
299	0.40	18690.675	18692.240	1.725
299	0.30	18690.835	18692.145	1.310
299	0.25	18690.920	18692.085	1.165
299	0.20	18691.000	18692.020	1.020
299	0.10	18691.220	18691.885	0.665
299	0.05	18691.309	18691.835	0.526
299	0.01	18691.465	18691.775	0.310
299	0.005	18691.520	18691.700	0.180
313	1.00	18690.570	18692.740	2.170
313	0.85	18690.655	18692.650	1.990
313	0.65	18690.805	18692.538	1.730
313	0.50	18690.945	18692.435	1.490
313	0.40	18691.055	18692.365	1.310
313	0.30	18691.160	18692.290	1.130
313	0.25	18691.230	18692.245	1.020
313	0.20	18691.300	18692.200	0.900
313	0.10	18691.500	18692.095	0.595
313	0.05	18691.850	18692.045	0.195

Table 5.1 (continued)

Temperature (K)	Concentration of Lead Nitrate (mol/dm^3)	^{207}Pb Resonance Frequency for Lead Nitrate (KHz)	^{207}Pb Resonance Frequency for Lead Perchlorate under corresponding Conditions (KHz)	Difference in Resonance Frequencies Δ Hz (KHz)
333	1.00	18691.030	18692.855	1.825
333	0.85	18691.100	18692.785	1.685
333	0.65	18691.205	18692.675	1.470
333	0.50	18691.330	18692.590	1.260
333	0.40	18691.420	18692.535	1.115
333	0.30	18691.550	18692.470	0.920
333	0.25	18691.595	18692.440	0.845
333	0.20	18691.675	18692.400	0.725
333	0.10	18691.850	18692.320	0.470
333	0.05	18692.050	18692.285	0.235

Table 5.2: Acidic Lead Nitrate Computing Results

Temperature (C)	A	B	C	K
15	0.5027	9.157	3.996×10^{-2}	3.024
26	0.5115	6.584	6.333×10^{-2}	3.346
40	0.5262	3.332	1.845×10^{-1}	4.744
60	0.5494	2.362	2.898×10^{-1}	4.875

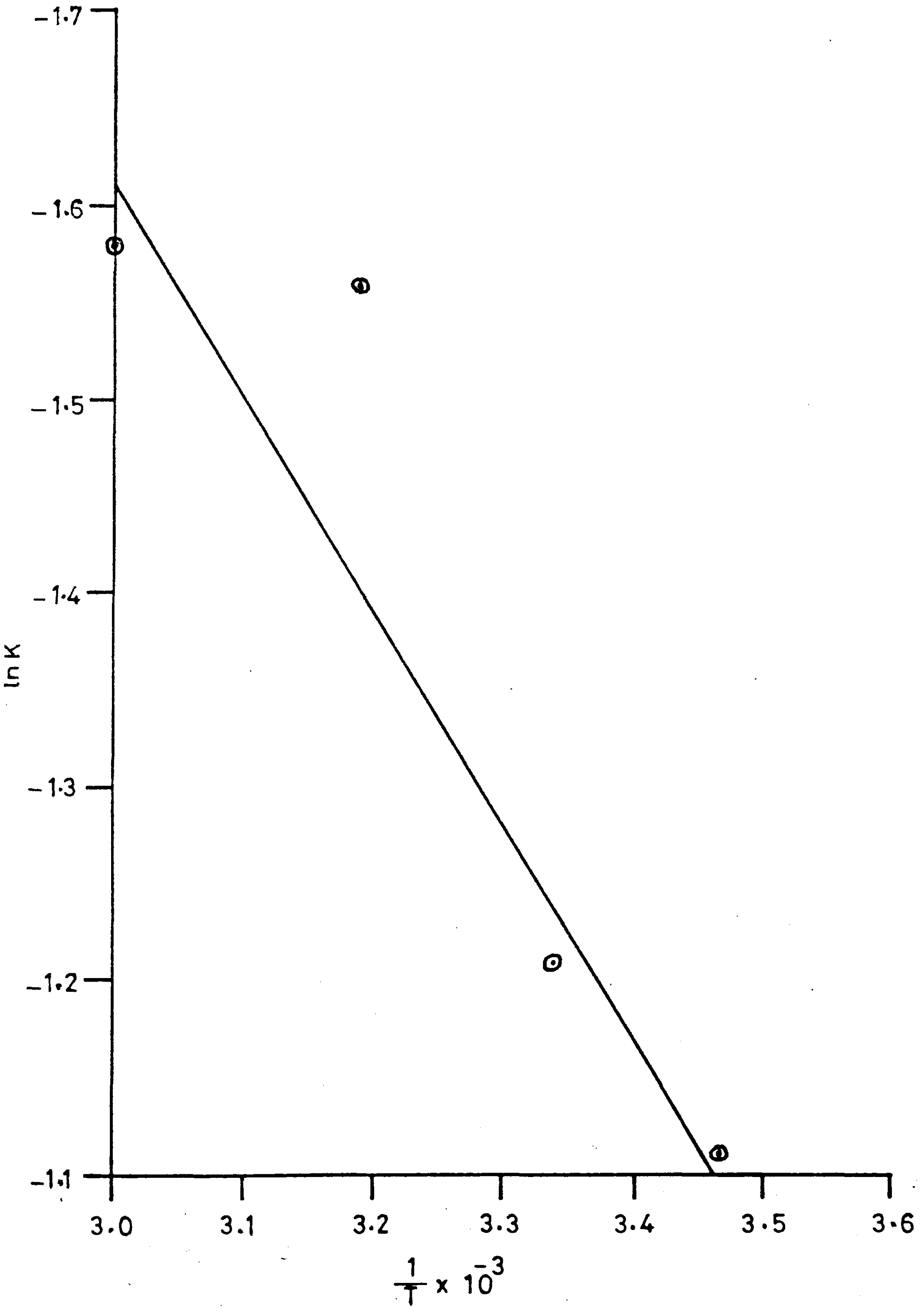
Data for Arrhenius Plot

lnK	$\frac{1}{T} \times 10^{-3}$
1.11	3.47
1.21	3.34
1.56	3.19
1.58	3.00

GRAPH 5.2

PLOT FOR lnK vs $\frac{1}{T}$

FOR ACIDIC LEAD NITRATE



5.6 Lead Acetate Data

There are several possible equilibria that could account for the processes occurring in acidic lead acetate solution. They are:

$$Pb^{2+} + OAc^- \rightleftharpoons PbOAc^+ \qquad (1)$$

where $\log K = \log Kc + 2.036 \left(\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - C\,I \right)$ at 298K

$$Pb^{2+} + 2OAc^- \rightleftharpoons Pb(OAc)_2 \qquad (2)$$

where $\log K = \log Kc + 3.054 \left(\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - C\,I \right)$ at 298K

and $I = 3[Pb^{2+}]$

A higher form of lead acetate, such as $Pb(OAc)_n^{(n-2)-}$ is not expected to be present, as $Pb(OAc)_2$ is used and the $[OAc^-]$ present is used up in making the complex, so that the concentrations of both Pb^{2+} (aq) and OAc^- fall rapidly if the value of K is high.

The basis of the calculation of the equilibrium constant for lead acetate relies on similar starting assumptions to the lead nitrate calculations, in that the ^{207}Pb resonance frequencies in lead acetate may be compared directly to the ^{207}Pb resonance frequencies in the corresponding concentrations in lead perchlorate.

Table 5.3 gives the experimental results.

Table 5.3: Lead Acetate in Acid Solution

Concentration (mol/dm^3)	$Pb(OAc)_2$ Resonance Frequency (KHz)	Corresponding $Pb(ClO_4)_2$ Resonance Frequency (KHz)	ΔKHz
At 299K			
1.000	18719.970	18692.650	27.32
0.500	18719.430	18692.300	27.13
0.400	18719.000	18692.220	26.78
0.250	18718.200	18692.080	26.12
0.100	18715.990	18692.910	24.08
0.050	18713.730	18691.840	21.89
0.025	18710.610	18691.800	18.81
0.010	18708.600	18691.770	16.83
0.005	18706.740	18691.750	14.99
At 313K			
1.000	18720.640	18692.740	27.90
0.500	18720.100	18692.440	27.66
0.250	18718.870	18692.250	26.62
0.100	18716.690	18692.100	24.59
0.050	18714.610	18692.050	22.56
0.005	18709.540	18692.000	17.54
At 288K			
1.000	18719.370	18692.580	26.79
0.500	18718.88	18692.220	26.66

Using the values for Δ Hz given in table 5.3, the following values of K have been obtained:

For equilibrium 1

Temperature (K)	$\frac{1}{T}\times10^{-3}$	K	lnK	B	C
288	3.47	82	4.41	30.0	0.1
299	3.34	133	4.89	28.4	0.3
313	3.19	144	4.97	29.0	0.3

For equilibrium 2

Temperature (K)	$\frac{1}{T}\times10^{-3}$	K	lnK	B	C
299	3.34	1500	7.31	29.0	0.1
313	3.19	17500	9.77	29.6	0.1

From the calculations, it appears that small changes in the values of B and C seem to have very little effect upon the value of K, so in this case, if K is quoted it is probably better to quote the conditions under which it was calculated, i.e. quote the B and C values.

The value of K appears to increase with increasing temperature, and it should be emphasised that the equilibria should be regarded as ligand replacement rather than mere association, e.g.:

$$Pb(H_2O)_n^{\,2+} + OAc^- \,(aq) \rightleftharpoons Pb(H_2O)_{n-2}OAc^+ + aq.$$

5.7 Cadmium Nitrate Data

Tables 5.4 and 5.5 show the data used and obtained for the equilibrium constant, K, calculations, at 299K, for various concentrations of acidic cadmium nitrate solutions. The calculations were carried out using the same assumptions as were used for the acidic lead nitrate data.

Table 5.4

Concentration of Cadmium Nitrate (mol/dm^3)	^{113}Cd Resonance Frequency for Cadmium Nitrate (KHz)	^{113}Cd Resonance Frequency for Cadmium Perchlorate under corresponding conditions	Difference in Resonance Frequencies Hz (KHz)
1.00	19872.870	19873.200	0.33
0.50	19873.020	19873.220	0.20
0.25	19873.110	19873.225	0.115
0.10	19873.170	19873.230	0.06
0.05	19873.170	19873.245	0.075

Table 5.5

Temperature (°C)	A	B	C	K
26	0.5115	1.085	8.469×10^{-2}	1.747

The value of K obtained from these calculations was in very good agreement with a value quoted in the literature by Masterton and Berka[129]. They found a value of K of 1.58 at 25°C.

APPENDIX

A. Other NMR Data

It was mentioned in table 1.1 that other nuclei apart from ^{113}Cd and ^{207}Pb were studied.

^{1}H and ^{13}C NMR data were used in the analysis of the ligands used. The numerical data have not been included, as the data were used only to confirm that the ligand was correctly supplied.

^{14}N was observed to see if the nitrogen in lead nitrate changed in linewidth or resonance signal with changing concentration. The signal was found to be constant under these conditions.

Similar studies to the ^{14}N studies were investigated with ^{35}Cl. The results are shown in table A.1. The resonance frequency of the ^{35}Cl signal did not change very much (0.011 KHz) with changing concentration. The signal due to perchlorate was found at a lower field than the signal due to the chloride ion.

^{19}F NMR data were collected on samples of cadmium fluoride. The results are shown in table A.2. The ^{19}F resonance signal appears to increase in frequency with decreasing concentration.

Some ^{33}S NMR experiments were carried out. The ^{33}S signal in most cases was found to be very broad and not very much information could be obtained from the experiments. The ^{33}S NMR data for lead dithionate and lead diethyldithiocarbamate are shown in table A.3.

The optimum parameters for studying the nuclei in this thesis, using the Jeol FX90Q spectrometer are shown in table A.4.

Table A.1

Chlorine (^{35}Cl) NMR data

At 299K

Compound	Concentration of Compound (mol/dm^3)	Resonance Frequency (KHz)
Lead Perchlorate in Acid Solution with 5% D_2O	1.75	8788.167
	1.50	8788.169
	1.08	8788.171
	0.50	8788.173
	0.25	8788.175
	0.05	8788.176
	0.025	8788.176
	0.01	8788.175
Perchloric Acid + 5% D_2O	0.05	8788.180
Cadmium Perchlorate in Acid Solution	1.00	8788.175
Cadmium Chloride in Acid Solution	1.00	8780.824

Table A.2

Fluorine (^{19}F) NMR Data

At 299K

Cadmium Fluoride in Aqueous Solution

Concentration of Cadmium Fluoride (mol/dm^3)	Resonance Frequency (KHz)
0.075	84297.780
0.050	84301.830
0.025	84301.910

Table A.3

Sulphur (^{33}S) NMR Data

Compound	^{33}S Resonance Signal (KHz)	Linewidth (Hz)	Number of Pulses
Lead Dithionate	6882.790	1200	110,000
Lead Diethyldithiocarbamate	6878.390	600	775,700

Table A.4 Optimum Parameters for obtaining Resonance Signals using JEOL FX90Q Spectrometer and 10mm Tunable Probe

Nucleus observed	^{207}Pb	^{113}Cd	^{13}C	^{14}N	^{19}F	^{35}Cl	^{33}S	^{1}H
Observation Frequency (MHz)	18.68-18.76	19.84	22.50	6.42	84.26	8.72	6.82	89.56
OBSET (KHz)	1 - 60	33-34.7	32.8-33.1	53.8	42.5-45.5	59.35	57.99	44.3-44.8
Band	3	3	3	1	5	1	1	5
Pulse width 1 (90° pulse) (μ s)	23	5	32	70	15	25	about 20	30
Pulse width 2 (180° pulse) (μ s)	46	10	64	140	30	50	-	60
Acquisition Time (s)	0.819	0.819	0.819	0.341	0.409	0.136	0.136	4.095
Pulse Delay (s)	1.0	1.0	0.1-1.0	0.10	0.25-1.5	0.5-1.0	1.0	0.89
Delay (μ s)	150-300	150-300	50-150	200-750	0.5	0.5	50	0.95
Frequency width (Hz)	5000-30000	5000-30000	5000	6002	20000	30000	30000	1000
Data points	8192	8192	8192	4095	8192	8192	8192	8192
Sample points	8192	8192	8192	4095	8192	8192	8192	8192
Irradiation set (KHz) (if used)	54.3	54.3	54.3-54.6	55.0	54.2	54.5	54.3	54.3

TABLE A.5

BRUKER PROGRAM TO MEASURE T_2

```
ED  T2

        1    ZE
        2    D1
        3    P1:A
        4    VD
        5    P2    PH2
        6    VD
        7    GO =  2
        8    WR    T2PBAC
        9    IF    T2PBAC
       10    IN = 1
       11    EXIT
```

Table A.6: Chemicals used and their sources

Compound	Chemical Formula	Relative Molecular Mass	Source
Lead Perchlorate	$Pb(ClO_4)_2.3H_2O$	460.14	Aldrich Chemical Co. Inc.
Lead Nitrate (Analar)	$Pb(NO_3)_2$	331.21	B.D.H.
Lead Acetate (Analar)	$(CH_3COO)_2Pb.3H_2O$	379.35	B.D.H.
Lead Tetrafluoroborate	$Pb(BF_4)_2$	380.80	Alfa Division Ventron
Thiourea (Thiocarbamide)	$CS(NH_2)_2$	76.12	M & B
Disodium Ethylenediamine-tetra-acetate	$C_{10}H_{14}N_2O_8Na_2.2H_2O$	372.24	M & B
Hexaphenyldilead	$Pb_2(C_6H_5)_6$	876.38	ABC
Sodium Dithionate	$Na_2S_2O_6.2H_2O$	242.14	B.D.H.
L-Cysteine Hydrochloride	$CH_2(SH)CH(COOH)NH_2HCl$	157.62	B.D.H.
Lead Tetraacetate	$Pb(OCOCH_3)_4$	443.39	Hopkin & Williams Ltd.
Tri-Normal-Propylplumbyl acetate	$C_{11}H_{24}O_2Pb$	395.19	ABC
Lead Thiocyanate	$Pb(SCN)_2$	323.35	Aldrich Chemical Co. Inc.
Lead II Citrate	$(C_6H_5O_7)_2Pb.3H_2O$	639.44	Fluka

TABLE A.6 (continued)

Compound	Chemical Formula	Relative Molecular Mass	Source
Lead Oxide	PbO	223.21	B.D.H.
Cadmium Chloride (Analar)	$CdCl_2.2\frac{1}{2}H_2O$	228.34	B.D.H.
Cadmium Fluoride (ultra pure)	CdF_2	150.40	Ventron
Cadmium Sulphate (Analar)	$3CdSO_4.8H_2O$	769.49	B.D.H.
Cadmium Iodide (Analar)	$Cd\,I_2$	366.21	B.D.H.
Lead Diethyldithiocarbamate	$((C_2H_5)_2NCSS)_2Pb$	503.73	Fluka
Cadmium Acetate (Analar)	$(CH_3COO)_2Cd.2H_2O$	266.52	B.D.H.
Sulphamic Acid	NH_2SO_3H	97.10	Hopkin & Williams.
Cadmium Nitrate	$Cd(NO_3)_2.4H_2O$	308.47	B.D.H.
Sodium Perchlorate (Analar)	$NaClO_4.H_2O$	140.46	B.D.H.
Sodium Nitrate	$NaNO_3$	84.99	B.D.H.
Sodium Acetate Anhydrous	CH_3COONa	82.04	B.D.H.
Nitric Acid	HNO_3	63.01	B.D.H.

TABLE A.6 (continued)

Compound	Chemical Formula	Relative Molecular Mass	Source
Hydrochloric Acid	HCl	36.46	B.D.H.
Perchloric Acid	$HClO_4$	100.46	B.D.H.
Acetic Acid	$CH_3(COOH)_2$	60.05	B.D.H.
Deuterium Oxide	D_2O	20.03	Koch-Light Laboratories Ltd.
Ethylene Diamine	$H_2NCH_2CH_2NH_2$	60.11	B.D.H.
Anthranilic Acid	$C_7H_7NO_2$ or $NH_2C_6H_4CO_2H$	137.14	B.D.H.
Ascorbic Acid	$C_2O_2(OH)C(OH)C_2H_2(OH)CH_2OH)$	176.12	B.D.H.
Citric Acid	$C_3H_4(OH)(COOH)_3 \cdot H_2O$	210.14	B.D.H.
Triethanolamine	$N(CH_2CH_2OH)$	149.19	B.D.H.
Triethylenetetramine	$(CH_2NHCH_2CH_2NH_2)_2$	146.24	B.D.H.

Table A.7

Computer program used in the calculation of equilibrium constants from NMR data

```
      PROGRAM KJM1

               KJM1 determines optimum values of:

               K,  the equilibrium constant for PB2+ + NO3   PBNO3+

               C,  the constant in the expression for activity coeff
                     -LN(F) = 0.5115*Z+Z-*(SORT(I)/(1+SORT(I)) -CI)

               B,  the proportionality constant between the experimental
                     NMR shift and the calculated function.

            The routine used is Simplex which minimises the square of the
            difference between the experimental and calculated NMR shifts
            by a Simplex method.

               INPUT: CARD1 ....... TITLE

                      CARD2 ....... NUMBER OF DATA POINTS (13)

                      CARD3 ....... DELTA HERTZ, CONCENTRATION
                                    OF PB(NO3)2 VALUES (8E10.4)

                      CARD4 ....... INITIAL GUESSES FOR B,K AND C.
                                    STEP - THE STEP SIZE FOR THE
                                           INITIAL SIMPLEX

      DIMENSION WN1(35)
      DIMENSION X(3)
      CHARACTER ITITLE *80,INFILE*20
      REAL I,K,NO3
      COMMON /B1/ DELHZ(30),CONC(30),NDATA
      EXTERNAL FNCT,MON
      WRITE(6,'(//10X,"INPUT FILE FOR DATA? ",$)')
      READ(5,'(A20)')INFILE
      OPEN(7,STATUS='NEW',RECL=137,FILE='OUT.LIS')
      OPEN(4,STATUS='OLD',RECL=80,FILE=INFILE)
      READ(4,100)ITITLE,NDATA
      READ(4,101)(DELHZ(J),CONC(J),TEMP,J=1,NDATA)
      READ(4,101)B,K,C,STEP
100   FORMAT(A80/13)
101   FORMAT(3E10.4)
      WRITE(7,1000)ITITLE,K,C,B
1000  FORMAT(//////1X,A80/20X,'GUESS VALUES',5X,'K= ',
     +F10.4,5X,'C= ',F10.5,5X,'B= ',1PE10.3)
```

```
                    INITIALISE FOR MINIMISATION ROUTINE
      X(1)=B
      X(2)=K
      X(3)=C
      N=3
      N1=25
                                MINIMISE
            CALL SIMPLEX(X,N,FNCT,STEP,MON,WN1,N1)
      S=FNCT(X,N)
      WRITE(7,1001)X,S
      WRITE(7,1002)
 1001 FORMAT (////50('*'),'RESULTS',50('*')/5X,'VALUES',5X,'B= ',
     11PE10.3,5X,'K= ',E10.3,5X,'C= ',E10.3/5X,'FUNCTION= ',E10.3)
 1002 FORMAT (//1X,'CONCENTRATION'4X,'IONIC STRENGTH',4X,
     +'PBNO3+',6X,'NO3-',6X,'PB2+',4X,'ACTIVITY COEFFICIENT'4X,
     +'DHZ OBSERVED',3X,'DHZ CALCULATED',3X,'DIFFERENCE')

      DO 20 J=1,NDATA
      A=CONC(J)
      Y=PBNO3X(X(2),CONC(J),X(3))
      I=3.*A-2.*Y
      NO3=2.*A-Y
      PB=A-Y
      QF=F(I,X(3))
      Z=QF*NO3*X(2)
      DCALC=X(1)*Z/(1.+Z)
      DIF=DELHZ(J)-DCALC
      WRITE(7,1003)CONC(J),I,Y,NO3,PB,QF,DELHZ(J),DCALC,DIF
 1003 FORMAT (4X,F7.4,10X,F7.4,3X,F10.6,3X,F10.6,F10.6,8X,F8.6,10X,
     +1PE10.3,6X,E10.3,6X,E10.3)
   20 CONTINUE
      STOP
      END
      FUNCTION PBNO3X(K,A,C)
```

Calculates equilibrium concentration of PBNO3+

Given K, the equilibrium constant
A, the initial concentration of PB(NO3)2
C, the constant in the activity coeff. function

A binary search method is used between zero and the total concentration

```
      REAL K,LNK,I
      IC=O
      XU=A
      XL=O.
      X=A/2.
            IF(K .LE. 0.)GOTO2
      LNK=ALOG(K)
      E PS=1.E=6*LNK
    1 I=3.*A-2.*X
      IC=IC+1
      IF(IC .GT. 1000)GOTO2
      PBNO3X=X
      Q=ALOG(X)-ALOG(A-X)-ALOG(2.*A-X)-ALOG(F(I,C))
      D=Q-LNK
      IF(ABS(D) .LT. EPS)RETURN
      IF (D .LT. 0.)GOTO10
      XU=X
      X=(XU-XL)/2. + XL
      GOTO 1
   10 XL=X
      X⅔(XU-XL)/2. + XL
      GOTO 1
  2   WRITE(6,1000)K,A,C,XU,XL,X,D
1000  FORMAT(///10X,'ERROR IN PBNO3X'/7(7X,1PE10.3)
 2    PBNO3X=10000.
      RETURN
      END
      FUNCTION F(X,C)
```

```
            F(X,C) is the activity coefficient of PB2+ at
            ionic strength X and with constant C
 IF(X .LT. 0.)THEN
      WRITE(6,'("ARGUMENT NEGATIVE IN F",E10.4)'
1)X
      F=0.
      RETURN
 ELSE
 S=SORT(X)
 F=10**(-2.046*(S/(1.+S)-C*X))
 RETURN
 ENDIF
 END
 FUNCTION FNCT(X,N)

            FNCT is called by E04CCF and calculates the square
            of the differences between the calculated and experimental
            NMR shifts using the current values of the three variables
            in X.  (B=X1,K=X2,C=X3)

 COMMON /B1/ D(30),CONC(30),NDATA
 DIMENSION X(N)
 REAL K,NO3,I
 B=X(1)
 K=X(2)
 C=X(3)
 S=0
 DO 1 J=1,NDATA
 Y=PBNO3X(K,CONC(J),C)
 I=3.*CONC(J)-2.*Y
 NO3=2.*CONC(J)-Y
 Z=F(I,C)*K*NO3
 DCALC=B*Z/1.+Z)
 S=S+(D( J)-DCALC)**2
```

```
1 CONTINUE
  FNCT=S
  RETURN
  END
  FUNCTION MON(I,FH,FL)

        THIS IS A DUMMY CALLED BY E04CCF

  CHARACTER *20 ISTR,ISTR1,ISTR2,ISTR3
  PARAMETER(ISTR='CALCULATING SIMPLEX ')
  IQ = DTS$CVT_L_TI(I,ISTR1)
  IQ= FOR$CVT_D_TE(FH,ISTR2,%VAL(5)
  IQ= LIB$PUT_SCREEN(ISTR//ISTR1//ISTR2//ISTR3,24,1)
  MON=0
  RETURN
  END
  INCLUDE '(UACA027A,TOOLS)SIMPLEX.FOR'
```

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