PROTON SPIN-LATTICE RELAXATION IN ACETONE-WATER MIXTURES

by

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We accept this thesis as conforming
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The work reported here is concerned with the measurement of the spin-lattice relaxation of protons in water, acetone, a D$_2$O - acetone mixture and various aqueous solutions of acetone. The theory to account for the decay rates has been outlined for a general case and has been applied in particular to acetone-water mixtures. The NMR technique has been described briefly. Temperature dependences of $T_1$ for all solutions have been investigated. It has been found that the relaxation in mixtures are slower than predicted by the theory.
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CHAPTER I

INTRODUCTION

In addition to mass and charge some nuclei also possess magnetic moments and angular momentum or spin. The magnetic moment is generally represented by \( \mu \). If an assembly of nuclei having magnetic moments is subjected to an external magnetic field, the tiny nuclear magnets experience a torque and tend to align themselves parallel to the field. Under suitable conditions these magnets can absorb energy from an oscillating radio frequency (RF) magnetic field. This absorption of energy gives rise to the Nuclear Magnetic Resonance (NMR) phenomenon.

In NMR experiments a nucleus is used as a magnetic probe to investigate the local magnetic effects, both intra and inter molecular, in a molecular system.

The largest observable component of nuclear angular momentum is \( I \) (measured in units of \( \hbar \) where \( \hbar \) is Plank's constant). \( I \), the spin number, is either integer or half integer. Since magnetic moment and angular momentum \( (I \neq 0) \) are collinear (A1), their lengths should always bear the same ratio \( \gamma = \mu / I \). \( \gamma \) is known as magnetogyric ratio.

The material in which the nuclear magnets are embedded is generally referred to as the "lattice", whether it be solid, liquid or gas (A2). The lattice
is characterised by the following properties:

(1). It is in equilibrium with itself, and

(2). Its heat capacity is much larger than that of the spin system.

A nuclear assembly with spin I has \(2I + 1\) distinct energy states which have the same energy and population in absence of an external magnetic field. These energy levels split up if an external magnetic field \(H_0\) is applied. The energy interval between two energy levels is \(\mu H_0/I\). However if we restrict ourselves to spin 1/2 particles, there are only two Zeeman levels corresponding to spins aligning with or against the applied magnetic field \(H_0\) as shown in figure I.

Let us consider a system of weakly interacting spins in thermal equilibrium with the lattice at temperature \(T\), the populations of the levels being proportional to the Boltzmann factor, i.e.

\[
\frac{n_+}{n_-} = \exp\left(2 \frac{\mu H_0}{kT}\right) - 1 = 1 + 2 \frac{\mu H_0}{kT} \quad \text{(to the first approximation)}
\]
Since \( n_+ \) is greater than \( n_- \), the difference of population \( n = n_+ - n_- \) gives rise to macroscopic magnetisation \( M_0 \) in the direction of applied magnetic field.

Since \( n = n_0 = (n_+ + n_-) \frac{\mu H_0}{kT} \) is the equilibrium value of excess no. \( n \)

a decrease in the excess number \( n \), in steady magnetic field, will correspond to a rise in "spin temperature". In case we consider a non-interacting spin system, \( T \) in equation 1 will be replaced by \( T_s \) where \( T_s = \text{spin temperature} \).

In NMR experiments a RF perturbation field is used which disturbs the thermal equilibrium of the system, thereby inducing transitions between the Zeeman levels, and thus tends to equalize the populations. In other words the RF field heats the spins. After the RF field is switched off, the spins come into thermal equilibrium with the lattice. The mechanisms responsible for the cooling of the spins are known as "spin-lattice relaxation" mechanisms.

Let \( W_+ \) and \( W_- \) be the upward and downward transition probabilities, then for equilibrium

\[
\frac{n_+ W_-}{n_- W_+} = \frac{n_- W_+}{n_+ W_-}
\]

Since each downward transition increases and upward transition decreases the excess number \( n \) by 2, the rate of change of \( n \) is given by the differential equation.

\[
\frac{dn}{dt} = 2n_- W_- - 2n_+ W_+
\]
\[
\frac{d\rho}{dt} = -2W(n-n_0)
\]
where \( W = (W_+ + W_-)/2 \).

\[
= -\frac{n-n_0}{T_I}
\]

where

\[
T_I = 1/2W
\]

If the applied field \( H_0 \) be in the z direction then (2.1) has the following form:

\[
\frac{d \langle I_z \rangle}{dt} = -\frac{\langle I_z \rangle - I_0}{T_I}
\]

where \( T_I \) is the characteristic time which the spin system takes to cool down to the lattice temperature. \( T_I \) is also called "spin lattice relaxation time".

A single time constant \( T_I \) does not always describe adequately the trend of nuclear spins towards the equilibrium with the lattice. Solution of (4.1) tells us that the approach is exponential. However, equation (3) describes the phenomenon correctly only if all the spins in the ensemble are alike.

Since spin 1/2 particles have only a magnetic moment associated with their spin, they can only interact with magnetic fields. Thermal equilibrium of the system then is attained only through the local magnetic fields present. The fluctuating local magnetic field at the site of a spin can chiefly be caused by following:

1. Fields due to other spins in the same molecule i.e. intra-molecular fields.
2. Fields due to spins of the other neighbouring molecules, i.e. inter-
molecular fields.

The extent of spin lattice relaxation depends upon two factors.
1. The magnitude of local fields and
2. The rate of fluctuation of local fields.

Thus both, inter and intra-molecular, contributions are responsible for spin-
lattice relaxation.

Since $T_1$ is a measure of the rate of exchange of energy between spins
and other degrees of freedom of the system, measurements of $T_1$ are capable
of giving detailed information about the molecular collisions, rotational
states and statistical properties of the molecular system.

The following chapter discusses the case of unlike spins in the en-
semble where a single time constant does not describe the recovery of the
system correctly. A theory appropriate to this situation will be outlined. It
has been applied to the particular case where the spins are alike but happen
to be in different chemical surroundings.

Chapter three gives a short description of pulsed NMR technique. The
electronic apparatus is also described. In chapter four the experimental re-
sults for mixtures of acetone and water are given and discussed.
CHAPTER II

THEORY

Since nuclei form the core in the atomic system, each nuclear magnet takes part in the random translational and rotational motion of a molecule. Consequently the local magnetic field, in a molecular system, is a rapidly fluctuating function of time. The component at the resonance frequency $\nu_0$ of the Fourier spectrum of this fluctuating field induces transitions between the energy levels in the same way as the RF field does.

If a system of $N$ identical particles with spin $1/2$ be considered, the only important interaction coupling the nuclear spins to the translational degrees of freedom is the magnetic dipole-dipole interaction between pairs of nuclear spins. The interaction Hamiltonian is

$$H_{dip-dip} = \frac{\gamma^2 \hbar^2}{\mu_0} \sum_{i<j} \left( \frac{I_i \cdot I_j}{r_{ij}^3} - \frac{3 (I_i \cdot \vec{r}_{ij})(I_j \cdot \vec{r}_{ij})}{r_{ij}^5} \right)$$  \hspace{1cm} (2.1)

where $\vec{r}_{ij}$ is the vector joining $i$th and $j$th nucleus with polar coordinates $r_{ij}, \theta_{ij}, \phi_{ij}$ and $I_i$ is the angular momentum operator for $i$th nucleus.

Following Bloembergen the expression for $T_1$ may be written down as

$$\frac{1}{T_1} = \frac{3}{2} \gamma^2 \hbar^2 I (I+1) \left[ J^{(e)}(\omega_z) + J^{(a)}(\omega_z) \right]$$  \hspace{1cm} (2.2)

where $\omega_z$ is the Larmor frequency for the nuclei with spin $I$ and $J^{(e)}(\omega_z)$
are the spectral densities given by

\[ J^{(k)}(\omega \tau) = \int_{-\infty}^{\infty} G^{(k)}(\tau) e^{-i\omega \tau} d\tau \]  

With the assumption that the random motion for the orientation of the vector \( \bar{r} \) is isotropic, \( G(\tau) \) is given by

\[ F^{(k)}_\tau F^{(k')}_\tau = \delta_{kk'} G^{(k)}(\tau) \]

where

\[ F^{(k)}_\tau = \frac{a_k Y^{(k)}_3(\Theta_{ij}, \Phi_{ij})}{\gamma_{ij}^3} \]

\( r_{ij}, \Theta_{ij}, \Phi_{ij} \) are dependent on time because of the dynamical motions of the spins.

However if the spins are unlike, a single relaxation time can no longer describe the trend of the system correctly and we get a system of coupled equations of motion instead of \( 1.4 \). Abragam (AI) has given the following equations to describe the coupling of two spin systems to each other

\[ \frac{d}{dt} \langle I_2 \rangle = -\frac{1}{t_{II}} \left( \langle I_2 \rangle - I_o \right) - \frac{1}{t_{II}} \left( \langle S_2 \rangle - S_o \right) \]  

\[ \frac{d}{dt} \langle S_2 \rangle = -\frac{1}{t_{III}} \langle I_2 \rangle - I_o - \frac{1}{t_{III}} \langle S_2 \rangle - S_o \]  

He defines the coefficients as below

\[ \frac{1}{t_{II}} = \gamma_k \gamma_s \bar{p} \bar{q} (s+1) \left[ \frac{1}{12} J^{(0)}(\omega + \omega_3) + \frac{3}{2} J^{(2)}(\omega_3) + \frac{3}{4} J^{(3)}(\omega_3 + \omega_5) \right] \]

\[ \frac{1}{t_{III}} = \gamma_k \gamma_s \bar{p} \bar{q} (s+1) \left[ -\frac{1}{12} J^{(0)}(\omega + \omega_3) + \frac{3}{4} J^{(2)}(\omega_3 + \omega_5) \right] \]
with similar equations for $T_{1}^{SS}$ and $T_{1}^{SI}$ by interchanging the indices I and S.

However, to take into account the contribution of the like spins, the intra-molecular and intermolecular terms, which appear in equation 2.2, have to be added in equation 2.6a to get the complete value of $T_{1}^{II}$. $T_{1}^{SS}$ can similarly be defined.

When the system 2.5 is solved under the initial condition, at $t = 0$,

$$\langle T_{2} \rangle = \langle S_{2} \rangle = 0$$

existing immediately after a 90° pulse, it is found that the solution is given by

$$\langle I_{2} \rangle - I_{0} = \frac{m_{I} + a_{IL} + S_{0} (m_{2} + a_{IL})}{m_{2} - m_{I}} e^{-\frac{m_{I} + a_{IL} + S_{0} (m_{2} + a_{IL})}{m_{2} - m_{I}} t}$$

$$\langle S_{2} \rangle - S_{0} = -\frac{a_{IL} I_{0} + S_{0} (m_{2} + a_{IL})}{m_{2} - m_{I}} e^{-\frac{a_{IL} I_{0} + S_{0} (m_{2} + a_{IL})}{m_{2} - m_{I}} t} + \frac{a_{IL} I_{0} + S_{0} (m_{2} + a_{IL})}{m_{2} - m_{I}} e^{t}$$

Experimentally, we measure the total proton magnetization

$$\left(\langle M_{1} \rangle + \langle M_{5} \rangle \right) - \left(\langle M_{1} \rangle + \langle M_{5} \rangle \right) = \gamma \hbar \left(\frac{a_{IL} I_{0} + S_{0} (m_{2} + a_{IL})}{m_{2} - m_{I}} \right) \frac{m_{I} t}{\alpha_{IL}}$$

$$+ \gamma \hbar \left(\frac{a_{IL} I_{0} + S_{0} (m_{2} + a_{IL})}{m_{2} - m_{I}} \right) \frac{n_{2} a_{21} - n_{2} (m_{2} + a_{IL})}{\alpha_{21}} e^{2.7}$$

with $\langle M_{5} \rangle = n_{5} \gamma \hbar \langle I_{5} \rangle$, $\langle M_{5} \rangle = n_{5} \gamma \hbar \langle S_{5} \rangle$

$n_{1}$ = number of I type of spins per cc., and

$$\alpha_{21} = \frac{1}{T_{1}^{II}}$$

$$\alpha_{22} = \frac{1}{T_{1}^{SS}}$$

$$\alpha_{II} = \frac{1}{T_{1}^{II}}$$

$$\alpha_{II} = \frac{1}{T_{1}^{II}}$$

$$m_{1}, m_{2} = \frac{(a_{II} + a_{22}) \pm \sqrt{(a_{II} - a_{22})^{2} + 4 a_{21} a_{22}}}{2}$$
In particular if $I$ and $S$ are like spins we have $I = S$

\[ \omega_I = \omega_S = \omega \]

\[ \gamma_I = \gamma_S = \gamma \]

and 2.6 reduces to

\[ \frac{1}{\tau_{11}} = \gamma^4 \kappa^2 I (I+1) \left[ \frac{1}{12} J^{(0)}(\omega) + \frac{3}{2} J^{(\omega)}(\omega) + \frac{3}{4} J^{(2\omega)}(\omega) \right] \]

\[ \frac{1}{\tau_{1s}} = \gamma^4 \kappa^2 I (I+1) \left[ -\frac{1}{12} J^{(0)}(\omega) + \frac{3}{4} J^{(2\omega)}(\omega) \right] \]

We obtain similar equations for $\frac{1}{\tau_{s1}}$.

With the assumptions that:

1. Motions of the molecules can be compared to that of a macroscopic sphere in a viscous liquid,

2. The diffusion equation is valid to describe the molecular motions,

3. Stoke's law relating viscosity and translational and rotational diffusion constants holds good,

Abragam gives the values of spectral densities as follows:

**FOR ROTATION**

\[ J^{(0)}(\omega) = \frac{1}{b^4} \cdot \frac{4}{15} \cdot \frac{\tau_c}{1 + \omega^2 \tau_c^2} \]

\[ J^{(2\omega)}(\omega) = \frac{1}{b^6} \cdot \frac{16}{15} \cdot \frac{\tau_c}{1 + \omega^2 \tau_c^2} \]

where $\tau_c$ is the correlation time defined as the order of time a molecule takes to turn through a radian, or to move through a distance comparable with
its dimensions. If the correlation time is much shorter than the Larmor period (which in case of liquids is satisfied) all spectral densities become independent of $\omega$ in the frequency range of interest. Thus under extreme narrowing

$$\omega \sim \gamma_c^2 < 1 \quad \text{and} \quad \frac{1}{T_1} = \frac{8 \pi I (I+1)(m-1)}{b^6} \frac{\alpha^3 \gamma}{kT}$$

$$= 2 \pi \frac{\gamma^4 k L}{b^6} (m-1) \frac{\alpha^3 \gamma}{kT} \quad \text{for spin } \frac{1}{2} \text{ particles.}$$

For translation, similar formulae are derived for the extreme narrowing case.

$$J^{(0)}(0) = \frac{32 \pi^2}{25} \frac{N \gamma}{kT}$$

$$J^{(0)}(\omega) = \frac{16 \pi^2}{75} \frac{N \gamma}{kT}$$

$$J^{(2)}(2\omega) = \frac{64 \pi^2}{75} \frac{N \gamma}{kT}$$

and for spin $1/2$ system

$$\left( \frac{1}{T_1} \right)_{\text{Trans. due to } I} = \frac{6 \pi^2}{5} \frac{\gamma^4 k L}{N I} \frac{\gamma}{T}$$

$$\left( \frac{1}{T_1} \right)_{\text{Trans. due to } S} = \frac{4 \pi^2}{5} \frac{\gamma^4 k^2}{N S} \frac{\gamma}{T}$$

$$\left( \frac{1}{T_1} \right)_{\text{Rot.}} = 2 \pi (m-1) \frac{\gamma^4 k^2}{b^6} \frac{\alpha^3 \gamma}{kT}$$

Hence $\frac{1}{T_1^{\text{II}}} = \text{sum of all equations in 2.13}$

$$= \frac{2 \pi}{5} \frac{\gamma^4 k^2}{k} \left[ 5 \frac{m-1}{b^6} \alpha_I^3 + 3 \pi N_I + 2 \pi N_S \right] \frac{\gamma}{T}$$
and \[
\frac{1}{T_{ls}^1} = \frac{2\gamma^I}{5} \frac{\gamma^2}{k} N^I \frac{\eta}{T}
\]  

with \( m \cdot 1 = \text{No. of spins in a molecule contributing to the intramolecular interaction.} \)

\( b_i = \text{Inter nuclear distance, between two i type spins, on a molecule.} \)

\( a_i = \text{effective radius of the rigid molecule which holds i type spins.} \)

\( \eta = \text{viscosity of the liquid.} \)

\( k = \text{Boltzmann constant.} \)

Values of \( I/T_{ls}^{ss} \) and \( I/T_{ls}^{si} \) can be written down by interchanging the indices I and S. In the present work I is used for the protons on acetone molecule and S for protons on water molecule.

Protons on different methyl groups in acetone are comparatively far apart and do not have significant contribution. Thus for acetone \( m=3 \) and for water \( m=2 \).
CHAPTER III

NMR PULSE TECHNIQUE AND EXPERIMENTAL APPARATUS

Pulse techniques were used, in this work, to study spin lattice relaxation time. Since this is a well established technique (H2), only an outline of the pulsed nmr methods is given below.

An assembly of nuclei having magnetic moments is placed between the poles of a magnet of field strength $H_z = H_0$. As already described in Chapter I, this gives rise to a resultant macroscopic magnetic moment $M_z = M_0$ (in the z direction). The magnetic field causes the magnetization vector $\vec{M}_z$ to precess about the field with angular frequency $\omega_0 = \gamma H_0$. A small coil with its axis at right angles to $H_0$ is wound round the sample and a linearly oscillating rf field $H_x = 2H_1 \cos \omega t$ is applied to the coil. This field is in effect equivalent to two magnetic fields of equal amplitude and rotating in opposite direction.

(I) $H_x = H_1 \cos \omega t$ \quad $H_y = H_1 \sin \omega t$

(II) $H_x = H_1 \cos \omega t$ \quad $H_y = -H_1 \sin \omega t$

Out of the two rotating fields only one effects the magnetic moment. Let us consider a coordinate frame rotating with the applied field. Then, if $\omega = \omega_0$, the magnetization vector is subjected to a constant torque $\vec{\tau} = \vec{M} \times \vec{H}$
Fig. 3.1
Induction tails
Facing Page -13-
in the rotating reference frame. Thus the effect of \( H_1 \) on \( M \) is to rotate it away from \( H_0 \) with an angular velocity \( \omega = \gamma H_1 \). If after \( t_w \) seconds the rf field is switched off, the angle of rotation of \( M \) is given by

\[
\theta = H_1 t_w
\]

If \( \theta = 90^\circ \), the pulse is known to be \( \pi/2 \) pulse.

The component of magnetization in the xy plane induces a voltage in the coil which is amplified, detected and displayed on the oscilloscope.

In the present work a train of \( \pi/2 \) pulses was applied in a time shorter than \( T_1 \). This ensured that the magnetization, in the z direction, at the end of the chain of pulses was zero. After \( t \) seconds a similar train was again applied and the height of the first induction tail was recorded. \( T_1 \) was worked out from

\[
A(t) = A(\infty)(1 - \exp(-t/T_1))
\]

where \( A(\infty) \) is the tail height after \( t > T_1 \). In this work \( t \geq 6 T_\gamma \) was taken to record \( A(\infty) \). A stop watch was used to measure the time. Induction tails at various times \( t \) and at a constant temperature were photographed on one single picture by multiexposure. Dumont camera type 2620 was used for this purpose. One of such pictures is shown on the back page.

The amplitudes of the tails were measured with an eyepiece which had a
FIGURE 1

BLOCK DIAGRAM OF THE APPARATUS
FACING PAGE 14
scale on the objective and could read up to 0.1 mm.

To make the pulse width exactly $\frac{T}{2}$, three identical pulses were used. Five echoes were observed, primary echo at time $t = 2T$, "stimulated echo" at $t = T + T$, "image echo" at $t = 2T - 2T$, and primary echoes at $t = 2T - T$ and $t = 2T$. The pulse width was adjusted until the fourth echo disappeared (H1).

APPARATUS

The block diagram of Fig. 1 illustrates the equipment used. The equipment may be subdivided into, more or less, independent units described below. All the circuit diagrams have been shown in Appendix A. The timing unit gives out pulses to trigger the gate which drives the RF power unit. It also triggers the scope. The circuit diagram is standard and needs no explanation.

The gated RF power unit puts out short and intense RF pulses. This is also a standard design, and has been essentially described by Bloom and Hahn (B3).

SAMPLE HEAD AND TEMPERATURE CONTROL SYSTEM

A picture of the sample head is shown on the back page. It has a coil, of copper tubing, of inner diameter nearly 1 1/4 inches. The sample coil is
mounted along the axis of bigger coil. It has 17 turns of No. 22 enamelled wire. This complete system is put inside a solid wooden block. The block just fits in the magnet gap. The sample is connected to the half wave line which feeds in the RF power. The half wave line is nearly 3 meters in length of RG 59U cable. Hot or cold water at a constant temperature is circulated in the outer coil. The specimen is heated by radiation. Location of the system inside the wooden block helps a great deal in minimizing the loss of heat to the surroundings.

A Colora, Ultrathermostat No. K-2027 was used to keep the temperature of the circulating water constant. The machine has a reservoir of 1.6 litres capacity and controls the temperature, from 0-100°C, within ±0.02°C of the desired value. It has a circulating pump attached to it which circulates water quite efficiently.

All temperature measurements of the sample were made by a copper-constantan thermocouple. Ice water slush was used as the reference bath. The EMF developed was measured with a Rubicon Co. potentiometer No. 57557. It could read correctly up to 0.05 mV.

The amplifier used is a model IF 2IBS LEL strip and is tuned to 30 Mc with a pass band of 2 mc. nearly. It has an input impedance of 300 ohms and can be matched to a single ended line of this impedance. It has a low noise and high stability. Bias for the amplifier was obtained from a Tektronix 160 power
supply. The detector IN295 is the final stage of the amplifier.

The magnet available was a permanent magnet (WM) of field strength nearly 7000 gauss. There was little choice for the frequency of the transmitter and it had to be matched to this field.
CHAPTER IV
RESULTS AND DISCUSSIONS

So far BPP Theory has been applied to various liquids to explain the relaxation phenomena. If this simple theory is good, it should be able to explain the relaxation mechanisms in mixture of such liquids which do not react chemically. If the results are explained, this will be a good way to study the nature of molecular interactions in mixtures. With this in mind the measurements of the spin lattice relaxation time $T_1$ in water, acetone, acetone-$D_2O$ mixture, and various percentages of acetone-water mixtures between $0^\circ$ - $50^\circ$C were performed. The acetone used was of spectrally analyzed quality and was dried by the sodium iodide method (LI). Water used, in all the samples, was doubly distilled. The acetone sample was purified using a getter technique (SI). All the specimens used were degassed and sealed under vacuum. A graph between known percentages (by wt.) of acetone in aqueous solutions and density was drawn. This graph was used to determine the percentage of acetone, in sample solutions, after pumping for a reasonable time. All density measurements were made with a picknometer. Results of measurements will be presented separately, followed by discussion. A comparison of the results is made with the theory outlined in Chapter II.

Before making $T_1$ measurements the behaviour of the amplifier was studied. A General Radio Standard signal generator (No. 805C) was tuned to the central frequency of the amplifier passband. The rf was modulated 100%
CALIBRATION CURVES FOR THE AMPLIFIER

FIGURE 4.1.
FACING PAGE 18
SPIN-LATTICE RELAXATION TIME OF WATER AS A FUNCTION OF TEMPERATURE

FIGURE 4.2
FACING PAGE 18

EXPERIMENTAL POINTS

VALUES OF SIMPSON & CARR

= T1 SEC.

TEMP. °C.

0  5  10  15  20  25  30  35  40  45
and fed into the amplifier through attenuators. The output of the generator was kept constant throughout the measurements. DC output of the amplifier was read on the 516 Tektronix scope, for various values of attenuation. The 0.5 v/cm scale of the scope was used during these measurements as it was intended to use the same scale during the experiment. Measurements were carried out for two different values of bias voltage. The graphs are shown in Fig. 4.1. It is seen that the graphs are quite linear between 0.5V and 3.0 volts output. Induction tail heights between 1 - 3 volts were taken for plots as most reliable. As a test $T_1$ in n-heptane was measured at two different temperatures and the values were found quite in agreement with those available, (M 2).

MEASUREMENTS IN WATER

Measurements of $T_1$ in water were carried out between 0° - 50°C. Fig. 4.2 shows the variation of $T_1$ as a function of temperature. The results obtained by Simpson and Carr (S 1) are also plotted for comparison. It is seen that the present experiment gives 19% higher value of $T_1$ at 0°C but at 50°C only 1% higher. The $T_1$ measurements reported here show a scatter of about ±5%.

It may be of some interest to mention here that in search of high purity water to be used, in this experiment, different sources were tapped. $T_1$ in distilled and demineralized water, after pumping for about eight hours, was found to be 2.9 sec at 21°C. Under similar conditions $T_1$ in doubly distilled
EXPERIMENTAL POINTS \( \frac{1}{T_1} \) VS \( \frac{\eta}{T} \) FOR WATER

THEORETICAL PLOT

VALUES OF SIMPSON & CARR

\( \frac{\eta}{T} \times 10^5 \)
water was found to be 3.3 sec. The latter type of sample was selected for use.

Simpson has mentioned that ordinary water was degassed and used in their work. This may be responsible for their lower results.

If it is assumed that (1) BPP theory for relaxation in liquids holds, (2) the Stokes law describing relationship between correlation time and viscosity is true, and (3) Stokes-Einstein prediction of the relation between viscosity and translation and self diffusion constant is correct, $T_1$ is expected to vary as $\eta/T$. It is seen (Fig. 4.3) that within the range of the temperature covered, the theoretical and experimental curves do not agree at all below $10^0\text{C}$.

**ACETONE**

Fig. 4.4 shows the variation of $T_1$ of protons in acetone as a function of temperature. The temperature range covered was $0^0 - 50^0\text{C}$. It is seen that $T_1$ remains more or less independent of temperatures between $13^0 - 50^0\text{C}$. This behaviour remains unexplained by BPP theory as may be seen from the plots of $\eta/T$ shown as a dotted line in Fig. 4.4. For this failure either intramolecular or intermolecular or both mechanisms may be responsible. Theoretically over 70% contribution in the relaxation mechanism comes from the intramolecular interactions. It is known, however, that rapid internal molecular motions can decrease the effectiveness of the intramolecular interactions (M 1). To take account of such factors in the complicated systems
studied here is difficult. Within the range of BPP theory, the intramolecular part depends upon $a^3/b^6$ and is therefore sensitive to the choice of 'a' and 'b'. Although 'b' is simply a proton-proton distance which is well defined and independent of temperature (at least in a small range), there is considerable ambiguity in deciding on a value for the "radius" of the molecule 'a'. It may be defined for a spherically symmetric molecule like methane but in case of a complex and big molecule like acetone the value of the radius of molecule depends upon how it is defined. The question may even arise as to whether 'a' is temperature dependent?

Measurements of Benedek and Purcell (B 2) show that the Stokes–Einstein relationship between viscosity and diffusion coefficient is, within experimental errors, correct for several hydrocarbons. The contributions of the intermolecular interaction to $T_1$ depend upon this. It is therefore suggested that the gross discrepancy between BPP theory and the temperature dependence of the experimental values of $T_1$ in acetone probably have their origin in the intra-molecular contribution.

**D$_2$O - ACETONE MIXTURE**

The mixture contains approximately 40% acetone by wt. or $2.3 \times 10^{22}$ protons per cc. (in pure acetone there are $4.7 \times 10^{22}$ protons/cc). A plot of $T_1$ vs temperature is shown in Fig. 4.4. Since the deuterons in D$_2$O have small magnetic moments, they do not contribute to the relaxation phenomenon. Also the intermolecular interaction between the protons of the acetone molecules is
considerably reduced. But there is no sign of increase in $T_1$. Some conclusions may be drawn from this.

The intramolecular forces are mainly responsible for relaxation in acetone. This is only true if no paramagnetic impurities such as $O_2$ were present in the mixture. However, the $D_2O$ used in this mixture was treated in an identical fashion to the $H_2O$ samples. It should be noted that the viscosity of the mixture is probably considerably increased as compared to that of pure acetone. It is known that acetone water mixtures have higher viscosities than pure acetone and $D_2O$ has a greater viscosity than $H_2O$. One thing is to be noted here that $T_1$ seems independent of temperature between $36^0$ - $50^0C$.

**AQUOUS SOLUTIONS OF ACETONE**

It has already been mentioned in Chapter II that, in case of unlike spins in an ensemble, a single characteristic time does not describe the trend of the system towards equilibrium. An appropriate theory for unlike spins has been outlined and it has also been shown there that, on the basis of BPF theory, the decay of the magnetisation vector is described by equation

$$2.8$$

which is rewritten below for convenience.

$$\left(M_s\right)_z + \left(M_0\right)_z - \left(M_{s0} + M_0\right)_z = \gamma \hbar \frac{\alpha \chi + S_0 (m_1 + a_{ll})}{m_1 - m_1} \frac{\eta \chi (m_1 + a_{ll}) - \eta a_{ll}}{\eta a_{ll}} e^{-\frac{m_1 t}{\alpha a_{ll}}}$$

$$+ \gamma \frac{\alpha \chi + S_0 (m_1 + a_{ll})}{m_1 - m_1} \frac{\eta \chi (m_1 + a_{ll}) - \eta a_{ll}}{\eta a_{ll}} e^{-\frac{m_2 t}{\alpha a_{ll}}}$$

The coefficients on the R.H.S. of the equation involve $T_1^{II}, T_1^{SS}, T_1^{Ss}, T_1^{ss}$ where for spin $1/2$ system
\[
\frac{1}{t_{II}} = \frac{2\pi}{5} \frac{g^2 k}{k} \left[ 5 (m-1) \frac{\alpha^3}{b^6} + 3\pi N_1 + 2\pi N_S \right] \frac{\eta}{T}
\]

\[
\frac{1}{t_{IS}} = \frac{2\pi}{5} \frac{g^2 k}{k} N_S \frac{\eta}{T}
\]

with similar expressions for \( \frac{1}{t_{IS}} \) and \( \frac{1}{t_{SS}} \).

To evaluate equation 2.8 we need numerical values of all the coefficients and exponents appearing therein. Equation 2.15 can easily be evaluated since all the parameters appearing are known but to solve 2.14 completely the value of 'a' is needed. However if \( N_S \) in 2.14 is made zero, one gets

\[
\frac{1}{t_{II}} = \frac{2\pi}{5} \frac{g^2 k}{k} \left[ 5 (m-1) \frac{\alpha^3}{b^6} + 3\pi N_1 \right] \frac{\eta}{T}
\]

which is an expression for \( T_I \) as a function of temperature, for like spins in a liquid and is known for acetone and water. If the value of \( T_I \) obtained experimentally is plugged in 4.1, it can immediately be solved for 'a'.

In the present work the value of \( T_I \) for water and acetone was taken from Fig. 4.4 at 25°C and substituted in equation 4.1. The values of 'b' for water and acetone used are 1.58Å° and 1.75Å° respectively. The molecular radii of acetone and water were thus found to be 1.33Å° and 1.5Å° respectively.

Once the values of the radii are known, \( T_{II}^I \) and \( T_{SS}^I \) can be evaluated. This in turn enables us to solve equation 2.8 completely. In other words for any acetone concentration in the solution and at any temperature the theoretical decay function of magnetization can be plotted.

At a constant temperature the viscosity of aq. solutions of acetone is
VISCOSITY VS % ACETONE IN AQUEOUS SOLUTION

$\eta \times 10^3$ POISE

$0^\circ C$

$4.4^\circ C$

$15^\circ C$

$23^\circ C$

$25^\circ C$

$35^\circ C$

$45^\circ C$

PERCENT ACETONE BY WT.

2.0 4.0 6.0 8.0
INDUCTION TAIL AMPLITUDE vs TIME

79% ACETONE
BY WT.
AT 45°C

EXPERIMENTAL PTS.

THEORETICAL PLOT

79% ACETONE
BY WT.
AT 4°-4°C
FIGURE 4.6B  FACING PAGE 23

INDUCTION TAIL AMPLITUDE VS TIME

48% ACETONE
BY WT.
AT 45°C

EXPERIMENTAL POINTS
THEORETICAL PLOT

48% ACETONE
BY WT.
AT 4.4°C
FIGURE 4-6 A  FACING PAGE 23

INDUCTION TAIL AMPLITUDE VS TIME

11% ACETONE
BY WT.
AT 45°C

EXPERIMENTAL POINTS

THEORETICAL PLOT

11% ACETONE
BY WT. AT 44°C
found to be nonlinear as a function of acetone concentration. This is shown in Fig. 4.5. It was thought worthwhile to investigate the behaviour of various concentrations of acetone in the solution as a function of temperature. Theoretical decay curves for two extremes of viscosity variations, i.e. 4.4°C and 45°C, are plotted in Fig. 4.6. Experimental points are also shown side by side for comparison. It is clear from the plots that the decay rates are slower in the mixtures than predicted by the theory.
3PULSE TIME-BASE
GENERATOR

TO SCOPE
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