

Nuclear Magnetic Resonance

Lisa M. Larrimore

The fundamentals of nuclear magnetic resonance (NMR) spectroscopy were explored on samples containing large numbers of protons. Mineral oil and diluted solutions of CuSO_4 were placed in a permanent magnetic field and exposed to transverse pulses of radiation at their resonant frequency with the TeachSpin Ps1-A NMR apparatus. For each sample, the spin-lattice (T_1) and spin-spin (T_2) relaxation times were measured, and it was shown that $T_2 < T_1$, as predicted. The relaxation times for the CuSO_4 solutions were found to decrease with increased concentration. The magnetic moment of the proton was measured to be $1.41(4) \times 10^{-26}$ J/T, which is 0.2% away from the theoretical value of 1.4106×10^{-26} J/T.

Introduction

Nuclear magnetic resonance spectroscopy, or NMR, is a frequently used technique for distinguishing between chemical structures. Molecules are placed in an external magnetic field and subjected to a transverse magnetic field that switches their spin orientations. The difference in energy between these orientations has an associated resonance frequency, which depends on both the identity of the nuclei and the strength of the external field. Because the strength of this field at the nucleus can be decreased by shielding effects from the surrounding electrons, the exact resonance frequency reveals information about the chemical bonds in the sample.

Any nucleus with an odd number of protons or neutrons has a net magnetic moment that can be observed through NMR; organic chemists therefore use NMR to map the carbon-hydrogen framework of molecules. An important application of NMR is magnetic resonance imaging (MRI), which looks at the location of hydrogen in the body. This technique allows doctors to monitor soft tissues that cannot be seen with X-rays, such as the heart, the brain, and joints [1].

Our samples were placed in the center of a permanent magnet, which provided a uniform external field in what will be called the z direction. The TeachSpin Ps1-A NMR apparatus exposed the samples to pulses of radiation at the resonance frequency in the x direction. When the magnetic moments of the atoms in the sample were not aligned with the z axis, precession resulted, inducing a measurable current in a pickup coil oriented along the x direction.

Since different chemical structures often affect the relaxation time of a sample in a magnetic field more than the resonance frequency, we examined two different relaxation times for each sample. The spin-lattice relaxation time, T_1 , is the characteristic time involved in going from the $| -z \rangle$ to $| +z \rangle$ spin orientation. The spin-spin relaxation time, T_2 , is the characteristic time involved in going from in-phase precession in the transverse directions to alignment with the original field direction.

Since mineral oil contains long hydrocarbon chains, it is easy to use in NMR measurements. Measurements were also made on water containing various concentrations of CuSO_4 to examine the effect of the concentration on the relaxation time.

Theory

The behavior of a proton in a magnetic field is governed by its magnetic moment,

$$\hat{\boldsymbol{\mu}}_p = \frac{1}{2} g_p \mu_N \hat{\boldsymbol{\sigma}}, \quad (1)$$

where g_p is the proton's gyromagnetic ratio, $\hat{\boldsymbol{\sigma}}$ is the Pauli spin operator, and μ_N is the nucleon Bohr magneton. μ_N , which determines the scale of the proton magnetic moment, is given by

$$\mu_N = \frac{e\hbar}{2m_p c} \quad (2)$$

where e and m_p are the charge and mass of the proton, and c is the speed of light [2]. The magnitude of the proton magnetic moment has been determined to be [3]

$$\mu_p = 2.7928\mu_N = 1.4106 \times 10^{-26} \text{J/T}. \quad (3)$$

The energy of a proton in a magnetic field \mathbf{B} is given by

$$\hat{H} = -\hat{\boldsymbol{\mu}}_p \cdot \mathbf{B} = -\frac{g_p e \hbar}{4m_p c} \hat{\boldsymbol{\sigma}} \cdot \mathbf{B}. \quad (4)$$

If the magnetic field is given by

$$\mathbf{B} = B_0 \hat{z} + B_1 \cos(\omega t) \hat{x}, \quad (5)$$

the Hamiltonian becomes

$$\hat{H} = -\frac{g_p e \hbar}{4m_p c} (B_0 \sigma_z + B_1 \cos(\omega t) \sigma_x). \quad (6)$$

The time-dependent Schrödinger equation is

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = -\frac{g_p e \hbar}{4m_p c} (B_0 \sigma_z + B_1 \cos(\omega t) \sigma_x) |\psi(t)\rangle. \quad (7)$$

If we define

$$\omega_0 = \frac{geB_0}{2mc}, \quad \omega_1 = \frac{geB_1}{2mc}, \quad \Omega = [(\omega - \omega_0)^2 + \omega_1^2]^{1/2}, \quad (8)$$

it can be shown [4] that the solution to the Schrödinger equation is

$$|\psi(t)\rangle = \exp\left(-i\frac{t}{2} [(2\omega - \omega_0) \hat{\sigma}_z - \omega_1 \hat{\sigma}_x]\right) |\psi(0)\rangle, \quad (9)$$

and the probability of spin flip from $|\psi(0)\rangle = |+\rangle$ is

$$P_{flip}(t) = |\langle - | \psi(t) \rangle|^2 = \frac{\omega_1^2}{2\Omega^2} (1 - \cos \Omega t). \quad (10)$$

Note that if $\omega \approx \omega_0$, the amplitude of this probability goes to ≈ 1 . The frequency of the transverse magnetic field that is required to flip the spin orientation is thus

$$\omega_0 = geB_0/2mc = 2\mu_p B_0/\hbar. \quad (11)$$

The probability of spin flip also depends on the duration of the pulse. If a short pulse at the resonant frequency is applied such that $\cos \Omega t = 1/2$, the magnetic moment of the protons will be rotated perpendicular to the original field (when measured, half the protons

will be in state $|+z\rangle$ and half in state $| -z\rangle$). This is known as a ‘90° pulse.’ When $\cos \Omega t = 0$, all the protons will flip to the $| -z\rangle$ state. This is known as a ‘180°’ pulse.

When $\hat{\boldsymbol{\mu}}_p$ is not aligned with $B_0\hat{z}$, there is a torque, $\hat{\boldsymbol{\mu}}_p \times \mathbf{B}$, exerted on the magnetic moment. The equation of motion is

$$\hat{\boldsymbol{\mu}}_p \times \mathbf{B} = \frac{\hbar}{2\mu_p} \frac{d\hat{\boldsymbol{\mu}}_p}{dt}. \quad (12)$$

Since $\mathbf{B} = B_0\hat{z}$, this leads to two coupled differential equations

$$\dot{\mu}_y = \frac{\hbar}{2\mu_p B_0} \dot{\mu}_x, \quad \dot{\mu}_x = -\frac{\hbar}{2\mu_p B_0} \dot{\mu}_y. \quad (13)$$

Note that using the previous definition for the resonance frequency, $\omega_0 = 2\mu_p B_0/\hbar$, both μ_x and μ_y obey

$$\ddot{\mu}_x + \omega_0^2 \mu_x = 0, \quad (14)$$

which means that $\hat{\boldsymbol{\mu}}$ precesses around the z axis at ω_0 . These spinning magnetic moments induce a measurable current in a pickup coil oriented transverse to the original field. This current is converted to a voltage output on the oscilloscope.

These precessing protons are dephased due to spin interactions with neighboring protons with a characteristic time T_2 . Since the magnetic field causing precession is not completely homogeneous, however, the protons actually dephase in much less time than the spin-spin relaxation time. The effect of the inhomogeneous field can be reversed by introducing a ‘180° pulse’ to reverse the direction of the magnetic moments, which brings the spins back into phase. This effect is known as spin echo, and it allows T_2 to be measured.

The exponential decay in the output signal when measuring the spin-spin relaxation time is caused by both the dephasing due to spin interactions and the realignment of magnetic moments with the constant magnetic field. Since the decay in signal when measuring the spin-lattice relaxation time is due only to the realignment of magnetic moments with the constant field, T_2 is always less than T_1 , and the two will be approximately equal in samples with few spin interactions.

Procedure

First, a sample of mineral oil was examined using the TeachSpin PS1-A NMR apparatus. By subjecting the sample to a single A pulse, the resonant frequency (at which the A pulse was maximized) could be determined. With the sample removed, a Hall probe gaussmeter was used to measure the strength of the permanent magnetic field in the region of the sample.

To measure the spin-lattice relaxation time, T_1 , a 180° A pulse was followed by a 90° B pulse. The height of the output signal due to the B pulse was measured as the time between the two pulses was increased. This was continued until the magnitude of the output signal decayed to zero (when half the protons were spin-up and half were spin-down) and then increased to close to its original value, representing the magnetization relaxing from $-M_0$ to M_0 .

To measure the spin-spin relaxation time, T_2 , a Meiboom-Gill pulse sequence was set up on the TeachSpin instrument. This basically created a 90° A pulse followed by a series of spin echo signals. The height and time of each echo signal was measured until they decayed to zero.

Since distilled water is a good source of protons, measurements were next made on samples of H_2O . Since the relaxation time for protons in pure water is very long, each sample of water contained a different concentration of a CuSO_4 solution. Measurements of T_1 and T_2 were made for samples of distilled water containing 100%, 50%, 10%, and 1% of the CuSO_4 solution, which itself had unknown concentration.

Results and Discussion

With the mineral oil sample in place, a single A pulse was created at the resonant frequency. The output displayed on the oscilloscope was downloaded to a computer and can be seen in Figure (1). By using the Hall probe gaussmeter, the magnetic field in the region of the sample was determined to be $B_0 = 0.3537 \pm 0.0005$ T. The 0.05 mT magnetic field of the earth can be neglected in comparison. The resonant frequency was measured as $\omega_0 = 15.088 \pm 0.001$

MHz. Using these measurements, Eq. (11) shows that the magnetic moment of the proton is

$$\mu_p = \frac{\omega_0 \hbar}{2B_0} = 1.414 \times 10^{-26} \text{ J/T}. \quad (15)$$

This is 0.2% different from the theoretical value given in Eq. (3), which is exactly the percent error in our measurements.

Figure (2) shows the data taken to measure T_1 for the mineral oil sample. The spin-lattice relaxation time was determined to be $T_1 = 60.0 \pm 0.3$ ms by fitting the data to an exponential function going from $-M_0$ to M_0 . Figure (3) shows the data taken to measure T_2 for the mineral oil sample. The spin-spin relaxation time was determined to be $T_2 = 57 \pm 1$ ms by an exponential fit.

The measurements of T_1 for the various concentrations of CuSO_4 in distilled water are shown in Figures (4-7), and the measurements of T_2 are shown in Figures (8-11). A summary of these relaxation times is shown in Table (1).

Table 1: Relaxation times T_1 and T_2 for CuSO_4 solutions

relative concentration	T_1 (ms)	T_2 (ms)
1%	87.6 ± 0.6	40 ± 1
10%	15.8 ± 0.1	16.0 ± 0.5
50%	2.71 ± 0.05	2.4 ± 0.1
100%	1.16 ± 0.02	0.80 ± 0.03

When the inverse of the relaxation times is plotted versus the relative concentration of CuSO_4 , the data can be fit with a quadratic function, as in Figure (12). While the exact nature of the relationship between concentration and relaxation time is unclear, it is clear that higher concentrations of CuSO_4 decrease the relaxation time of the protons in distilled water. Furthermore, as expected, T_2 is greater than T_1 for all solutions (except the 10% solution, for which the difference is less than their absolute errors). The fact that the difference between the two relaxation times is generally small means that the additional factor for T_2 , the dephasing due to spin interactions, is not as significant as the realignment of protons with the constant magnetic field.

Conclusion

To see how NMR can be a useful technique for distinguishing between chemical structures, the basic theory behind the technique was explored. Two types of samples, mineral oil and CuSO_4 solutions, were studied because of their large numbers of protons. All samples were placed inside a permanent magnetic field of constant strength, causing them to align in the $|+z\rangle$ state along the field direction. Using the TeachSpin Ps1-A NMR apparatus, the nuclei were exposed to a transverse magnetic field at the frequency corresponding to the energy difference between the $|+z\rangle$ and $|-z\rangle$ states, causing them to change spin orientation. When they were aligned in the x - y plane, precession caused by the permanent magnetic field in the z direction could be measured on an oscilloscope through a pickup coil.

By measuring the strength of the permanent magnetic field in the region of the sample and the resonant frequency at which the mineral oil response was greatest, the magnetic moment of the proton could be determined. The measured result of $1.41(4) \times 10^{-26}$ J/T was 0.2% different from the theoretical value of 1.4106×10^{-26} J/T.

The spin-lattice and spin-spin relaxation times were also measured for the mineral oil and for each concentration of CuSO_4 solution. Since the spin-spin relaxation time is caused by the same effect as the spin-lattice relaxation time as well as an additional factor, it was always found to be less than the spin-lattice relaxation time. The difference between the two was generally not significant, which means that the extra factor (dephasing due to spin interactions) contributed little. It was also found that the relaxation times for the CuSO_4 solutions decreased with increased concentration, due to greater proton interactions.

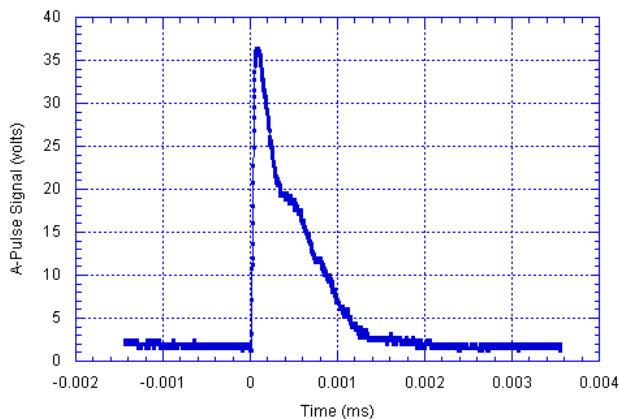


Figure 1: Measured output on oscilloscope for mineral oil subjected to a 90° A pulse.

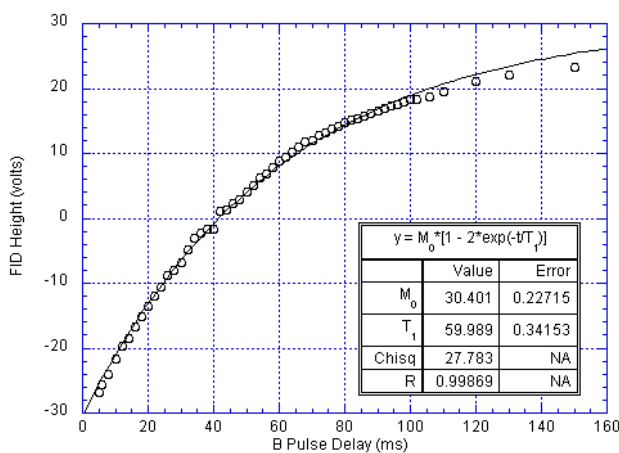


Figure 2: Magnetization versus time for mineral oil sample subjected to 180° A pulse followed by 90° B pulse. The spin-lattice relaxation time is $T_1 = 60.0 \pm 0.3$ ms.

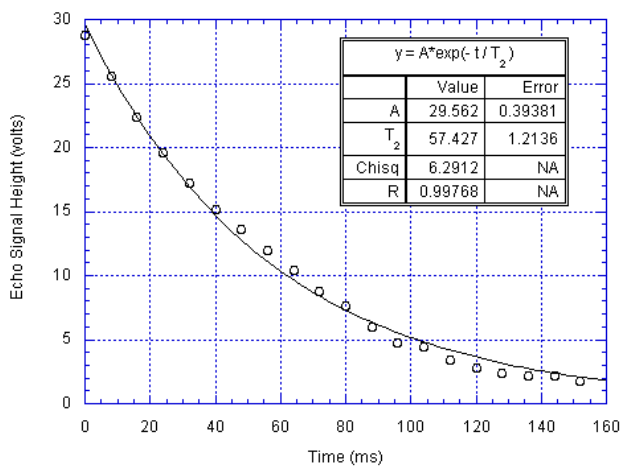


Figure 3: Echo signal height versus time for mineral oil sample subjected to a Meiboom-Gill pulse sequence. The spin-spin relaxation time is $T_2 = 57 \pm 1$ ms.

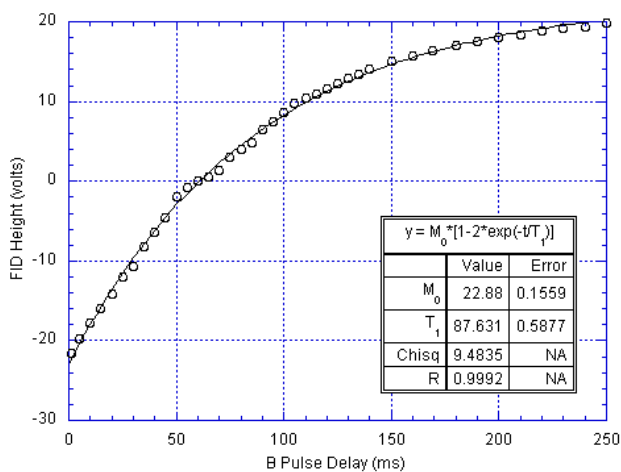


Figure 4: Magnetization versus time for 1% solution of CuSO_4 subjected to 180° A pulse followed by 90° B pulse. The spin-lattice relaxation time is $T_1 = 87.6 \pm 0.6$ ms.

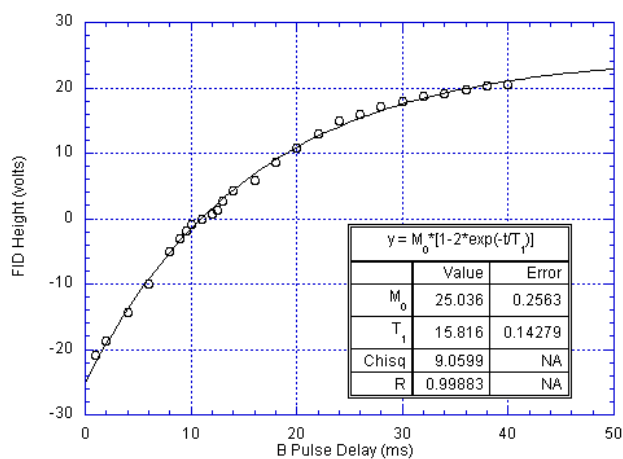


Figure 5: Magnetization versus time for 10% solution of CuSO_4 subjected to 180° A pulse followed by 90° B pulse. The spin-lattice relaxation time is $T_1 = 15.8 \pm 0.1$ ms.

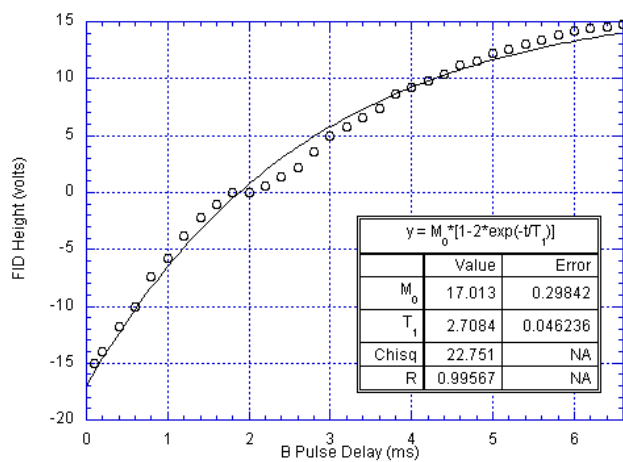


Figure 6: Magnetization versus time for 50% solution of CuSO_4 subjected to 180° A pulse followed by 90° B pulse. The spin-lattice relaxation time is $T_1 = 2.71 \pm 0.05$ ms.

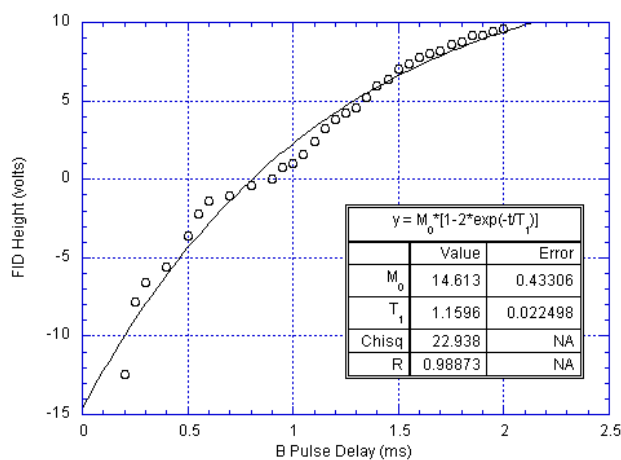


Figure 7: Magnetization versus time for 100% solution of CuSO_4 subjected to 180° A pulse followed by 90° B pulse. The spin-lattice relaxation time is $T_1 = 1.16 \pm 0.02$ ms.

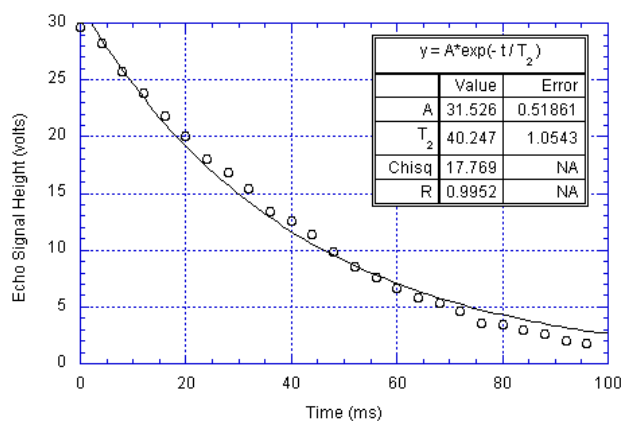


Figure 8: Echo signal height versus time for 1% solution of CuSO_4 subjected to a Meiboom-Gill pulse sequence. The spin-spin relaxation time is $T_2 = 40 \pm 1$ ms.

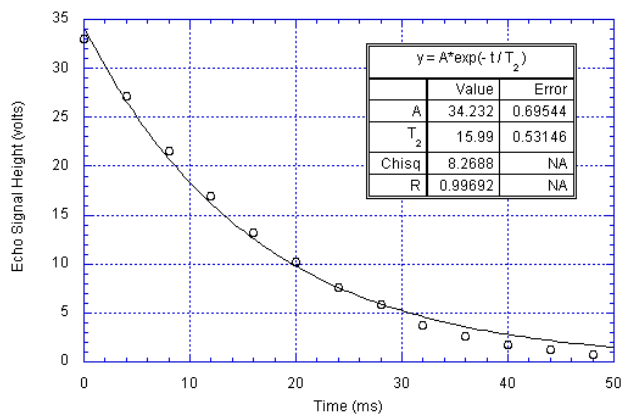


Figure 9: Echo signal height versus time for 10% solution of CuSO_4 subjected to a Meiboom-Gill pulse sequence. The spin-spin relaxation time is $T_2 = 16.0 \pm 0.5$ ms.

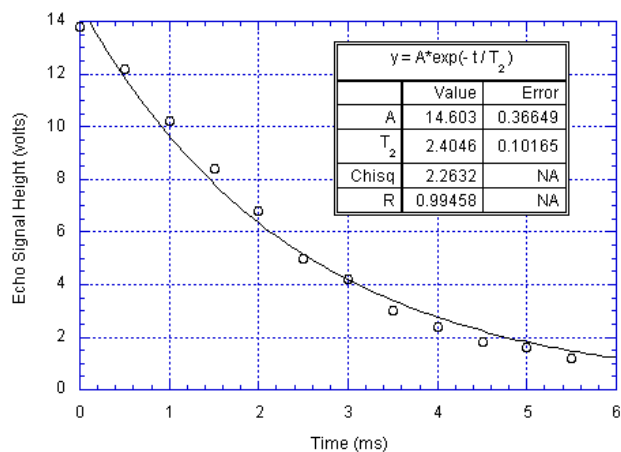


Figure 10: Echo signal height versus time for 50% solution of CuSO_4 subjected to a Meiboom-Gill pulse sequence. The spin-spin relaxation time is $T_2 = 2.4 \pm 0.1$ ms.

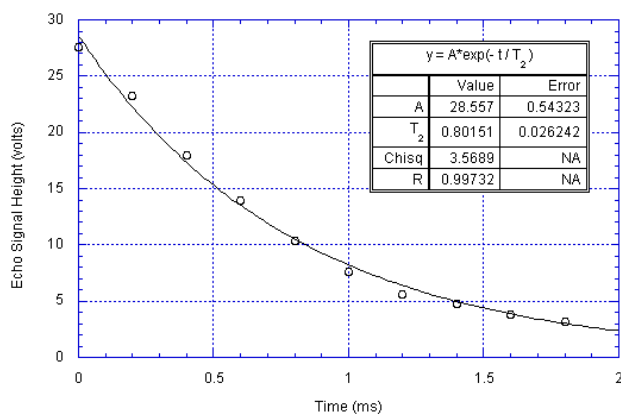


Figure 11: Echo signal height versus time for 100% solution of CuSO_4 subjected to a Meiboom-Gill pulse sequence. The spin-spin relaxation time is $T_2 = 0.80 \pm 0.03$ ms.

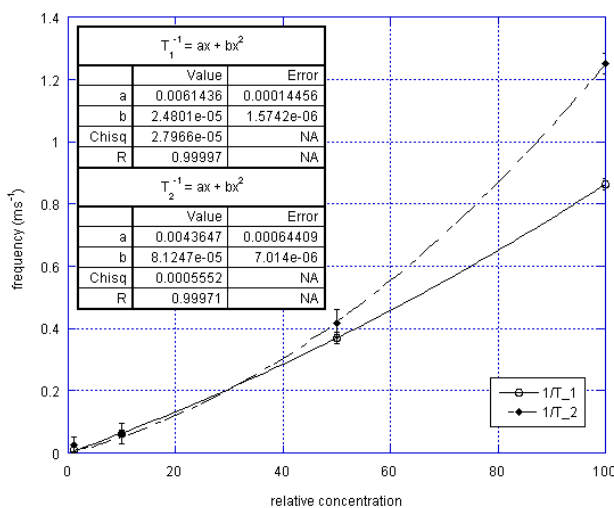


Figure 12: The inverse of T_1 (open circles) and T_2 (solid diamonds) plotted versus the relative concentration of CuSO_4 , with error bars of magnitude $\Delta t/t^2$. Both relaxation times are fit to quadratic functions.

References

- [1] J. McMurry, *Organic Chemistry* (Brooks/Cole, New York, 2000), Chap. 13.
- [2] R. Shankar, *Principles of Quantum Mechanics* (Plenum Press, New York, 1994), Chap. 14.
- [3] *Nuclear Magnetic Resonance*, lab handout, Swarthmore College (2001).
- [4] J. Boccio, *Quantum Mechanics: Mathematical Structure and Applications in the Physical World* (2000), Chap. 10.