

ENPH 453 Advanced Engineering Physics Lab

Lab 2: Pulsed NMR

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Executive Summary

The purpose of this experiment was to study nuclear magnetic resonance (NMR) of hydrogen, and understand how the presence of paramagnetic ions impacts the relaxation times. A spin-echo sequence was used to determine the spin-spin and spin-lattice relaxation times for distilled water and a 0.166 mM Iron (III) Chloride solution.

The T1 relaxation times were determined by varying the period, T, of the spin-echo sequence while holding the delay, τ , constant. T1 was found to be (0.08 ± 0.01) s for water and (0.03 ± 0.02) s for the iron solution. The T2 relaxation times were determined by varying τ while holding T constant. T2 was found to be (0.0030 ± 0.0002) s for water and (0.004 ± 0.005) s for the iron solution. The R squared values were 0.94 and 0.59 for the T1 values for water and the iron solution respectively, and 0.99 and 0.69 for T2 values for water and the iron solution respectively. T1 and T2 for water and the Iron solution are plotted with error bars in Figure 1.

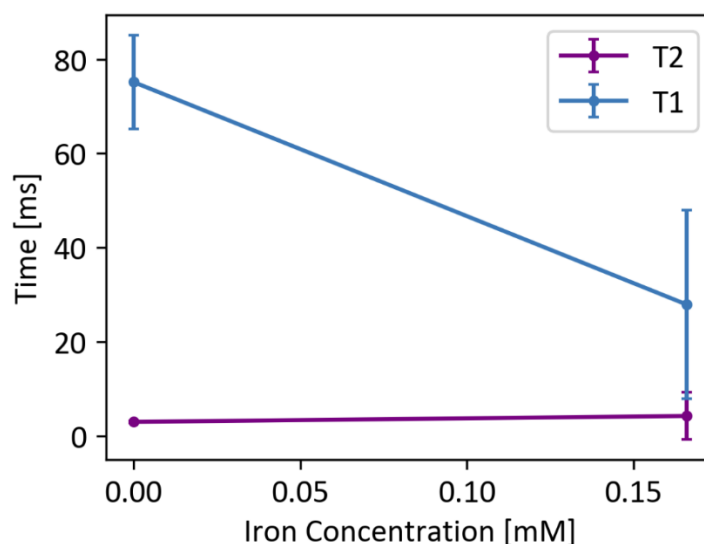


Figure 1: T1 and T2 relaxation times for 0.166 mM Iron (III) Chloride Solution and distilled water. Vertical error bars are included, horizontal error bars are not included due to unknown uncertainty of the Iron (III) Chloride solution concentration.

The T1 and T2 values found experimentally could not be compared absolutely to those found in literature due to differences in experimental setup in other studies. Instead, the trends were compared. Both relaxation times were both expected to decrease in the presence of paramagnetic ions, which agreed with experimental data for T1, and for T2 within error. T1

Uncertainties in this experiment were present due to equipment precision and uncertainty in the fit of experimental data. Results could be improved in future studies by taking more data points to produce better fits and by increasing the signal to noise ratio of the spin-echo. Considering multiple Iron (III) Chloride solutions would also provide better insight into how T1 and T2 vary in the presence of paramagnetic ions.

Abstract

In this investigation, the nuclear magnetic resonance (NMR) of hydrogen was studied. A spin-echo sequence was used to determine the spin-spin and spin-lattice relaxation times for distilled water and compared to those of a 0.166 mM Iron (III) Chloride solution. This was done with the goal of understanding how the presence of paramagnetic ions impacts NMR. The apparatus included a pulse generator, a waveform generator, an RF controlled magnetic coil, several amplifiers and filters, and an oscilloscope.

T1 was found to be (0.08 ± 0.01) s for water and (0.03 ± 0.02) s for the iron solution. T2 was found to be (0.0030 ± 0.0002) s for water and (0.004 ± 0.005) s for the iron solution. The R squared values were 0.94 and 0.59 for the T1 fits for water and the iron solution respectively, and 0.99 and 0.69 for T2 fits for water and the iron solution respectively.

T1 and T2 relaxation times were expected to decrease in the presence of paramagnetic ions due to interaction between the nuclear spin and the magnetic field produced by the paramagnetic ions in the Iron (III) Chloride solution. This was true for experimental data for T1, and for T2 within error, as expected. The experiment verified the relationship between relaxation times and the presence of paramagnetic materials.

Introduction and Theory

Pulsed NMR

Pulsed Nuclear Magnetic Resonance (NMR) is a powerful technique that can be utilized for purposes such as Magnetic Resonance Imaging (MRI) [1]. Hydrogen is most commonly studied in NMR due to its abundance in nature and large magnetic moment.

The hydrogen nucleus is composed of a single proton, which has a magnetic spin of one half. In the presence of a magnetic field, the proton aligns itself either with or against the magnetic field, and the energy of the nucleus depends on the orientation relative to the magnetic field [2].

In this process, a material begins in a constant magnetic field with proton spins aligned. A radio frequency (RF) pulse is applied at the Larmor frequency, which excites the proton spins to a state that is perpendicular to the direction of the field. These spins then precess and eventually return to their equilibrium position with the field, causing the nuclei to emit electromagnetic radiation that is detected by a receiver coil. The observable signal is known as free induction decay (FID). Figure 2 illustrates proton spin re-alignment in a field that begins with spins aligned.

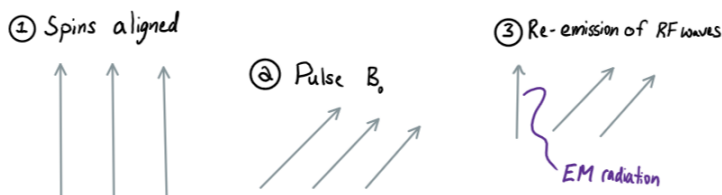


Figure 2: Illustration of the emission of electromagnetic (EM) radiation as the proton spins return to equilibrium.

The resonance conditions for most nuclei can be found in tables, which should then be used to determine the radio frequency required for resonance in a magnetic field [3]. For this experiment, a frequency of 15 MHz corresponds to a magnetic field of 0.35 T. This means protons exposed to a 15 MHz field can absorb this energy resonantly when embedded in a 0.35 T field.

Relaxation Times

The spin-lattice relaxation time (T_1) is related to the longitudinal magnetization of the proton [2]. It describes the characteristic time for the proton spin to lose its energy and return to its equilibrium state along the direction of the magnetic field. The spin-spin relaxation time (T_2) is related to the transverse magnetization. It characterizes the rate at which the magnetization dephases and decays perpendicular to the direction of the magnetic field due to interaction with the surrounding medium. T_1 is typically longer than T_2 [4]. T_2 measurements provide better indication of the nature of the medium when compared to T_1 since the decay is due to interaction with the medium.

The Spin-Echo Sequence

As transverse magnetization rotates about the z-axis, it will induce a current in a coil located about the x-axis, which can be used to accurately determine T_1 and T_2 by applying a pulse sequence [5]. In this experiment, a spin-echo sequence is used. This involves the application of a $\pi/2$ pulse, which puts the spins in the x-y plane [3]. After a time τ , the spins will have precessed around the z axis, becoming out of phase as a consequence of inhomogeneity in the field. Because the field is inhomogeneous, the spins will dephase. A π pulse is then applied to flip the spins and allow the spins that precessed further to catch up with those that precessed less. By measuring the strength of the echo at a time 2τ , the effect of magnetic field inhomogeneity is removed.

Using the spin-echo sequence, the signal intensity S can be written using Equation 1 [6].

$$S = k\rho \exp\left(-\frac{\tau}{T_2}\right)\left(1 - \exp\left(-\frac{T}{T_1}\right)\right) \quad (1)$$

Where S is the intensity of the signal, k is a constant, ρ is the proton density, τ is the echo time, and T is the period of the sequence.

Determining T_1 and T_2

To determine T_1 , the period T can be varied while holding other variables constant. This allows Equation 1 to be effectively reduced to Equation 2 below, which we can fit using experimental data to determine T_1 .

$$S = A * \left(1 - \exp\left(-\frac{T}{T_1}\right)\right) + C \quad (2)$$

Where A and C are constants. Similarly, to determine T_2 , the delay between pulses τ can be varied while holding other variables constant, reducing Equation 1 to Equation 3 below.

$$S = A * \exp\left(-\frac{\tau}{T_2}\right) + C \quad (3)$$

The presence of paramagnetic materials is expected to decrease relaxation times based on literature [7].

Apparatus and Procedure

Apparatus

The experimental apparatus consists of the equipment outlined in Table 1, and assembled according to the diagram seen in Figure 3.

Table 1: Summary of the equipment used and baseline settings to observe spin echo signals.

Component	Baseline Component Setting
Agilent 81L04A 80 MHz Pulse-Pattern Generator	Pulse length of $10\ \mu\text{s}$ and $20\ \mu\text{s}$ for the $\pi/2$ and π pulses; starting delay of 1 ms; starting period of 1 s; offset of 700 mV and amplitude of 1.4 V; ensure pulses are added at Output 1
Agilent 33220A 20 MHz function/arbitrary waveform generator	Signal with frequency of 15.2 MHz at an amplitude of 1.2 V p-p; output turned on
Amplified Research 75AP250 RF amplifier	Set to a quarter gain, corresponding to the third tick
Agilent 6554A DC power supply	Set voltage to 60 V and current to 1 A so that current is the limiting factor and can be varied with the dial
RF-controlled magnetic coil	Controlled by the power supply described above; field strength of $\sim 0.35\ \text{T}$
Lakeshore 425 Gaussmeter	Turn on
Variable Amplifier	Specifications of component not noted; set to gain of 20
Tektronix TBS 1052B-EDU Digital Oscilloscope	Channel 1 to a vertical scale of 10 mV/div; trigger off second pulse using the B trigger set to trigger one event after A; set trigger to Normal mode

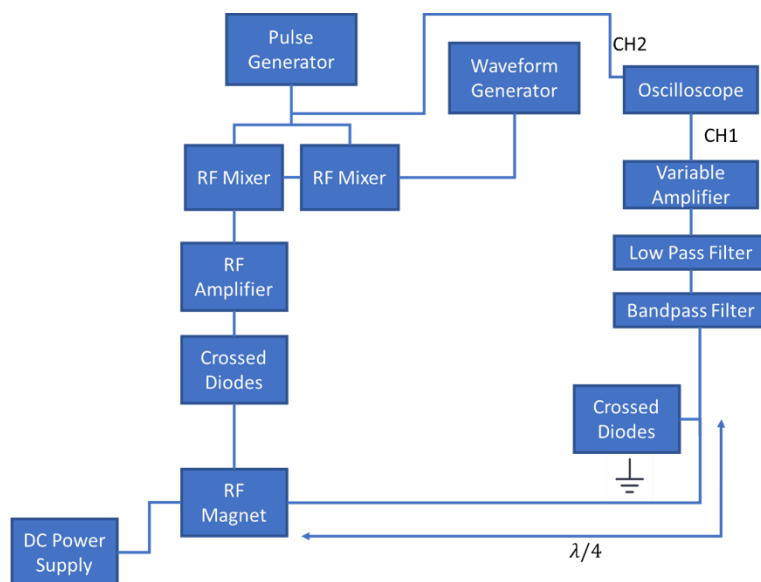


Figure 3: Diagram of apparatus setup. The component specifications and settings can be found in Table 1, with the exception of the filters, RF mixers, and crossed diodes which are explained below instead.

The pulse generator is set to produce a $\pi/2$ and π pulse by setting the pulse lengths to $10\ \mu\text{s}$ and $20\ \mu\text{s}$. This is mixed twice with a steady 15.2 MHz frequency signal produced by the waveform generator. The frequency of 15.2 MHz is used because it is the frequency required to transition between the ground state and excited state for a hydrogen proton embedded in a $\sim 0.35\ \text{T}$ field. The signal is amplified, then diodes are crossed to prevent reflection. A coil then picks up the response, which is transmitted across a length corresponding to one quarter of a wavelength so any bounce-back interferes destructively. Diodes are crossed again to prevent reflection before the signal is passed through a bandpass filter to remove anything outside of the 15.2 MHz range of interest. Finally, the filtered signal is sent through a lowpass filter and amplified once more with the variable amplifier before being displayed through the oscilloscope.

Procedure

The experimental procedure is as follows:

1. Set up the equipment as described in Table 1, placing a vile of distilled water into the electromagnet.
2. Start at a τ value of 1 ms and period of 1 s, with the voltage set to 60 V and current set to 1 A so that current is limiting.
3. Slowly vary the current until a spin echo is seen, and make note of the reading on the Gaussmeter at this current. Anticipate seeing an echo at a current of approximately 2.2296 A for both water and the iron solution. This should be consistent for all values of τ – significant changes in the current setting to observe spin echo indicate a hysteresis effect, which is also evident in a change in the reading on the Gaussmeter. To resolve this, reset the magnet by reducing the current back to 1 A and varying the current to find the spin-echo signal again. The reading on the Gaussmeter should reset to the value you recorded. Note that the reading of the Gaussmeter varies based on how it is positioned on the electromagnet and so should not be moved.

4. Once the spin echo has been found, modify the averaging on the oscilloscope to 64 to improve the quality and stability of the signal.
5. Insert USB to oscilloscope and turn on data logging. Export a single waveform to the USB, taking care to note the τ and T values in addition to the solution concentration for each waveform.
5. Vary the parameter of interest, T in the case of T1 study and τ in the case of T2 study, exporting the data to USB at each interval. Appropriate values of T and τ are described in data collection.
6. Create an iron solution or use one of the pre-made solutions found at the lab station. Due to time constraints and limited chemical equipment, the pre-made solution of concentration 0.166 mM was used in this experiment.
7. Repeat steps 1-5 with the iron solution/s.

Data Collection

The period, T, and delay between pulses, τ , were varied to collect data for determining T1 and T2 respectively. All other settings described in Apparatus were held constant. The studies described below were conducted for distilled water in addition to an iron solution with concentration of 0.166 mM.

Due to time constraints, custom solutions were not prepared and rather the provided one at the lab bench was used. This solution was known to have a concentration of $10^{20} \frac{\text{ions}}{\text{mL}}$ with an unknown uncertainty. This was converted to a molar concentration of 0.166 mM by dividing by Avogadro's constant, 6.022×10^{23} .

T1 Study

To determine T1, the delay was held constant at 3 ms while the period was varied from T=1 s to T=0.1 s at 0.1 s decrements, then additional measurements were taken at 0.075, 0.05, 0.025, 0.05 s. No measurements were taken beyond this as distortion of signal was evident at T<0.05 s, due to the length of the period relative to pulses and delays. The delay of 3 ms was chosen because it produced a clear echo in T2 studies.

At each T value, the channel 1 output was exported via USB. Plots of the raw data for water and iron are seen in Figure 4 and Figure 5 below.

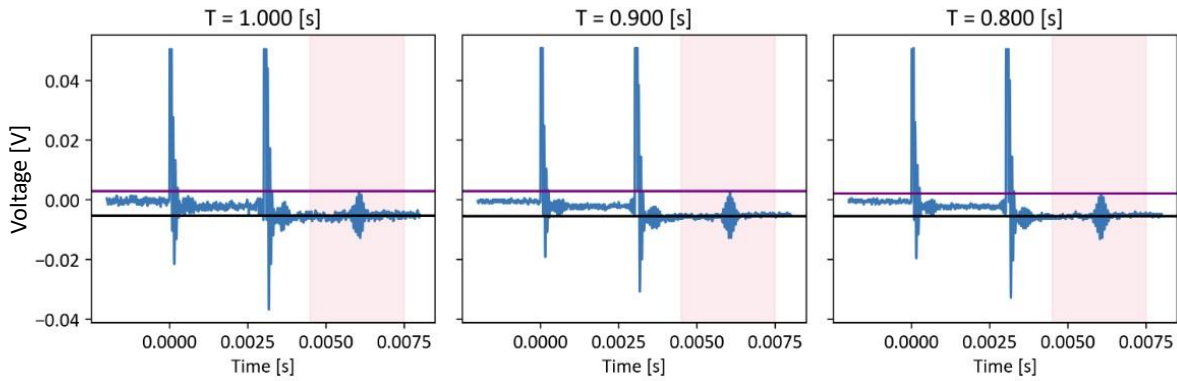


Figure 4: Waveforms for water at $T=1, 0.9, 0.8$ s with τ held constant at 1ms. Horizontal bars show the average voltage of the spin echo (black) and the maximum amplitude of the spin echo (purple). This illustrates a drop in average voltage after each of the $\pi/2$ and π pulses. The region highlighted in pink contains the spin echo, located 2τ from time 0.

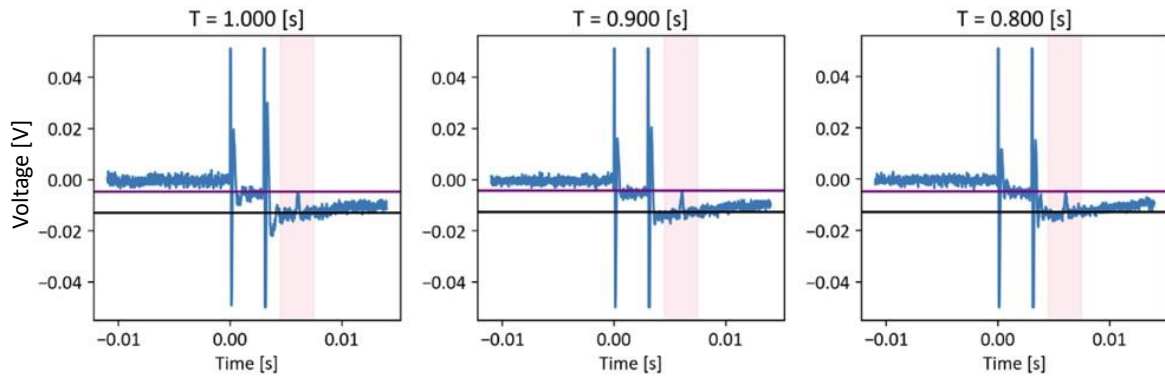


Figure 5: Waveforms for the iron solution at $T=1, 0.9, 0.8$ s with τ held constant at 1ms. Horizontal bars show the average voltage of the spin echo (black) and the maximum amplitude of the spin echo (purple). The region highlighted in pink contains the spin echo, located 2τ from time 0.

T2 Study

To determine T_2 , the period was held constant at 1 s and the delay was varied. For water, τ was varied from 1 ms to 21 ms at 2 ms increments. Beyond 21 ms, the amplitude of the spin echo was small and difficult to observe. For the iron solution, τ was varied from 1 ms to 5 ms at 0.5 ms increments. The lower range of delays was required for the iron solution because the initial spin echo amplitude was smaller than that of water, meaning the τ value for which the spin echo is too small to analyze is lower.

At each τ value, the oscilloscope scale was adjusted to ensure the echo was in view before exporting the channel 1 output via USB. Plots of the raw data for the T_2 study for water and 0.166 mM solution of iron are seen in Figure 6 and Figure 7 below.

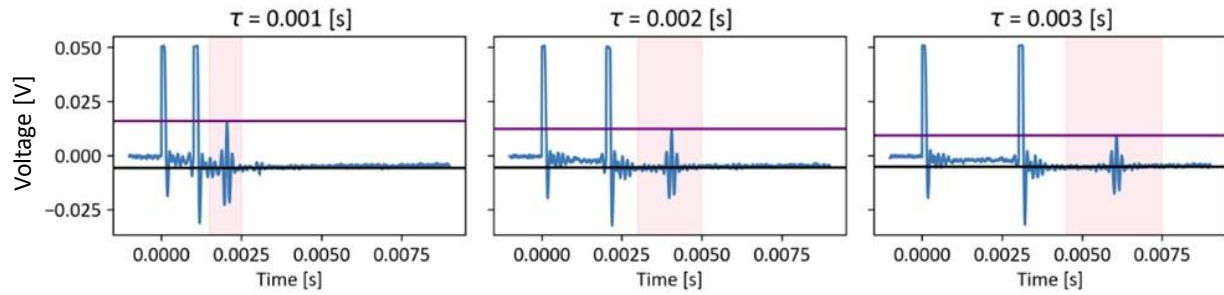


Figure 6: Waveform for water at period of 1s varying τ . Horizontal bars show the average voltage of the spin echo (black) and the maximum amplitude of the spin echo (purple). The region highlighted in pink contains the spin echo, located 2τ from time 0.

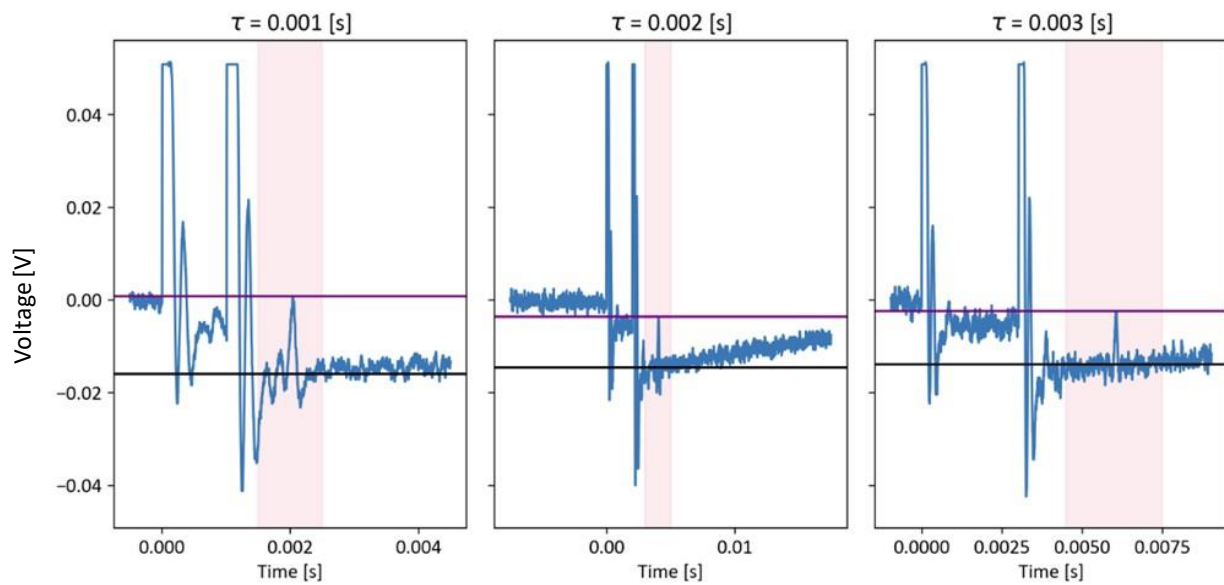


Figure 7: Waveform for iron with a period of 1 s varying τ . Horizontal bars show the average voltage of the spin echo (black) and the maximum amplitude of the spin echo (purple). The region highlighted in pink contains the spin echo, located 2τ from time 0.

Data Analysis

Data analysis was conducted to calculate T1 and T2 from the experimental data shown in Data Collection.

Uncertainties

Uncertainties were present due to equipment precision in addition to uncertainty in the fit of experimental data. Uncertainty on voltage readings is 50 microvolts and the uncertainty on time is 5 microseconds due to the precision of the oscilloscope. The uncertainty on T1 and T2 values come from the covariance matrix of the fit.

T1 Study

To calculate T1, the amplitude of the spin echo for period-dependent data was plotted against T and fit using Equation 2. The T1 value is the inverse of the exponential parameter of the fit curve. The R

squared value for the T1 fit for water was calculated to be 0.94 and for the iron solution was calculated to be 0.59. An R2 value of 0 means the curve fits the data no better than a horizontal line going through the mean of all Y values, so the water fit is significantly better than that of the iron solution.

To determine the amplitude of the spin echo, the range of interest was first selected from the data by looking at two times the delay since time zero, which is where one expects to see the echo. The maximum voltage reading in this range was subtracted by the average voltage in this range to account for any offset. This was repeated to obtain the amplitude of the echo for each T value. The amplitudes are plotted with the curve fits for water and the iron solution in Figure 8 and Figure 9 below.

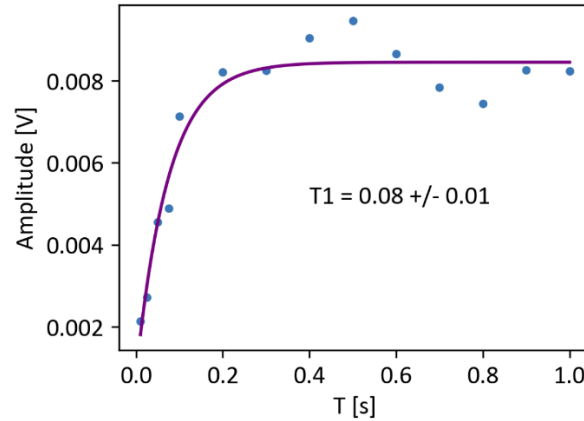


Figure 8: Amplitude of spin echo plotted as a function of period at a constant delay of $\tau=0.3$ s for distilled water. A curve fit is included, and seen to fit the data well visually. T1 was determined from this fit to be $0.08 \text{ s} \pm 0.01 \text{ s}$. Vertical error bars with constant magnitude of 50 microvolts and horizontal error bars with constant magnitude of 5 microseconds are included but difficult to see.

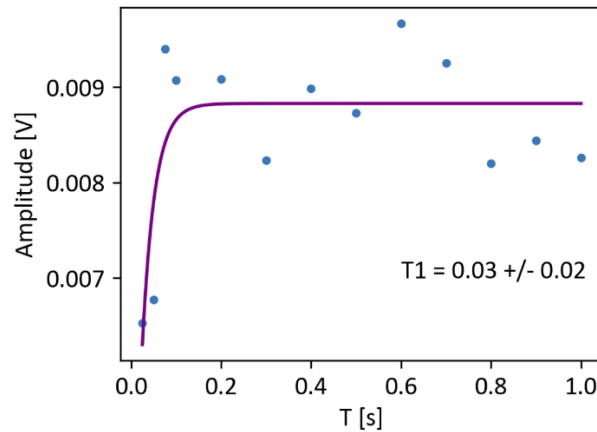


Figure 9: Amplitude of spin echo plotted as a function of period at a constant delay of $\tau=0.3$ s for iron solution. A curve fit is included, but the quality of the fit is low as the data does not follow the expected trend. T1 was determined from this fit to be $0.03 \text{ s} \pm 0.02 \text{ s}$. Vertical error bars with constant magnitude of 50 microvolts and horizontal error bars with constant magnitude of 5 microseconds are included but difficult to see.

T2 Study

To calculate T2 for a given solution, the amplitude of the spin echo for tau-dependent data was plotted as a function of τ and fit using Equation 3. The T2 value is the inverse of the exponential parameter of the fit curve. The uncertainty on the T2 value comes from the covariance matrix of the fit. The R squared

values were calculated to be 0.99 and 0.69 for T2 fits for water and the iron solution respectively, indicating the water fit is very good and the iron solution fit is satisfactory.

Spin echo amplitudes were determined as done in the T1 study. The amplitudes are plotted with the curve fits for water and the iron solution in Figure 10 and Figure 11 below.

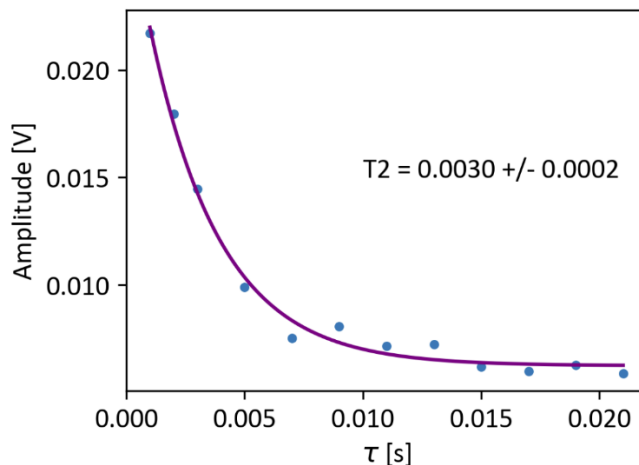


Figure 10: Amplitude of spin echo as a function of tau for distilled water, with curve fit. T2 was determined to be (0.0030 +/- 0.0002) s. Vertical error bars with constant magnitude of 50 microvolts and horizontal error bars with constant magnitude of 5 microseconds are included but difficult to see.

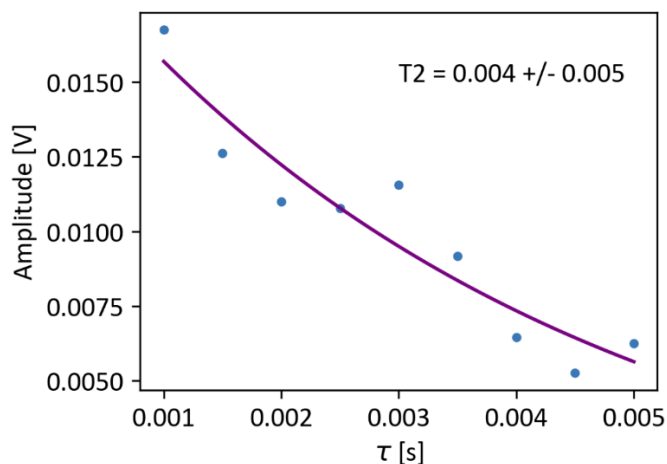


Figure 11: Amplitude of spin echo as a function of tau for iron solution, with curve fit. T2 was determined to be (0.004 +/- 0.005) s. Vertical error bars with constant magnitude of 50 microvolts and horizontal error bars with constant magnitude of 5 microseconds are included but difficult to see.

Comparison of T1 and T2 for Water and Iron Solution

The calculated T1 and T2 values for distilled water and the iron solution can be compared to understand how the presence of iron impacts NMR. These values are plotted in Figure 12 below.

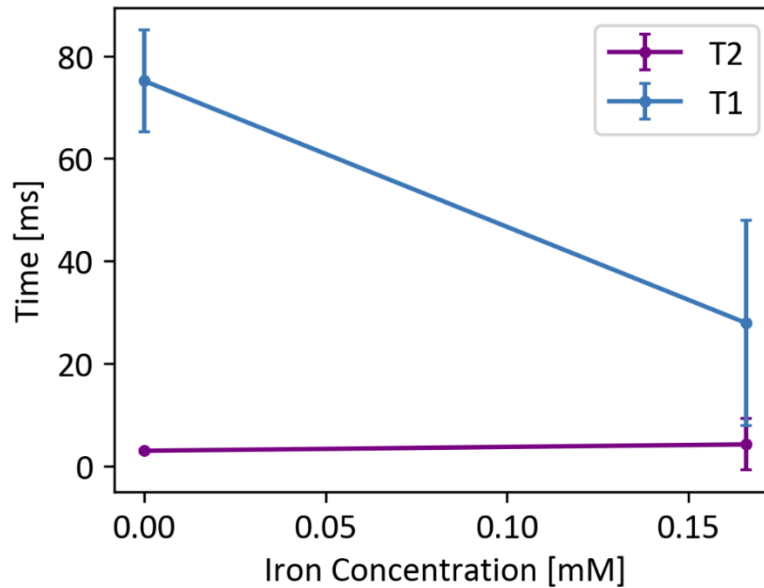


Figure 12: T1 and T2 relaxation times for water (concentration 0) and the 0.166 mM iron solution. Vertical error bars are included but some are difficult to see due to varying sizes. Horizontal error bars are not included due to the unknown uncertainty of the iron solution.

The plot shows that the T1 value decreased in the presence of iron, and the T2 value increased. However, the increase in T2 has a high uncertainty due to size the error bars on the T2 value and is not very meaningful; T2 for the iron solution could have truly decreased if the uncertainty is taken into account.

Results and Discussion

T1 Study

T1 was found to be (0.08 ± 0.01) s for water and (0.03 ± 0.02) s for the iron solution. A previous study that used iron solutions consisting of $FeCl_3$ dissolved in HCl found a T1 value on the order of 0.5 s for a solution of concentration between 0.1 mM and 0.2 mM, and 2.5 s for deoxygenated water [8]. This study cannot be directly compared to the results obtained in this experiment due to the different choices of iron solution and the water being deoxygenated, however one can draw the conclusion that the T1 time is expected to decrease in the presence of iron in the solution. With this in mind, the T1 values found exhibit the expected trend. T1 was also found to be larger than T2 for both water and the iron solution, which agrees with theory.

T2 Study

T2 was found to be (0.0030 ± 0.0002) s for water and (0.004 ± 0.005) s for the iron solution. The mentioned student using iron solutions consisting of $FeCl_3$ dissolved in HCl found a T2 value on the order of 0.3 s for a solution of concentration between 0.1 mM and 0.2 mM, and 1 s for water [8]. From this, one anticipates the T2 time will decrease in the presence of iron in the solution. The calculated T2 values agree only when the error on the values are taken into account.

A potential source of error came from the method of data collection for the iron solution, which has an uncertainty value an order of ten larger than that of water. In the experiment, the data points for $\tau =$

0.001, 0.003, and 0.005 s were taken before the other points and are seen to have slightly higher magnitude than the others in Figure 11. It is expected that this occurred due to a variation in the magnetic field strength in the time between measurements, resulting in higher intensity readings for the three data points taken first. This significantly impacted the quality of the fit. The dataset should have been retaken to test this theory, if time allowed.

Additionally, the range of τ values studied for the iron solution was much smaller than that of water (maximum of 0.005 s for iron vs 0.021 s for water), which impacted how defined the exponential curve was. This was done because the echo signal was smaller for iron, and since the increased delay decreases echo amplitude, it was difficult to study at high delays. A higher gain could have been used to amplify the signal and allow for more measurements at higher tau values, but it is important to note these would have to be converted to be consistent with other measurements at lower gain.

Conclusion

The T1 and T2 values found in this experiment followed the expected trend within error that T1 and T2 would decrease in the presence of iron. This is because of the interaction between the nuclear spin and paramagnetic ions [7]. As the number of paramagnetic ions is increased, the nuclear spin becomes coupled more with the magnetic field produced by the paramagnetic ions in the Iron (III) Chloride solution. This interaction contributes to the decrease in relaxation times. T1 was also found to be larger than T2 for both water and the iron solution, which agrees with theory [6].

It was expected that both the T1 and T2 relaxation times would decrease in the presence of iron. This was found to be true for T1, and for T2 within uncertainty. This can be explained by the large error on the calculated T2 value, particularly for the iron solution, which came from the scattered raw data.

For future studies, the quality of the fit to the experimental data could have been improved by changing the period at smaller decrements to get more data points. An averaging time of 128 rather than 64 would have also produced a more precise signal. Resetting the current to 1 A in between measurements would have eliminated any inconsistencies in magnetic field or hysteresis effects that could have impacted data quality. Finally, considering multiple Iron (III) Chloride solutions would provide better insight into how T1 and T2 vary in the presence of paramagnetic ions.

References

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