

Nuclear Magnetic Resonance and the Measurement of Relaxation Times of Acetone with Gadolinium

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1 Introduction

Nuclear magnetic resonance (NMR) is a spectroscopic technique frequently employed by chemists to elicit the structures of chemicals, especially organic molecules, in a liquid or solid form. In the field of medicine, where a 2 dimensional version of NMR termed magnetic resonance imaging (MRI) is employed, this technique has also had significant impacts on the development of non-invasive diagnosis of diseases.

First introduced in the 1940's by Felix Bloch and Edward Purcell to measure the magnetic moment of nuclei in liquids and solids, NMR is based on protons in a nucleus having an intrinsic spin angular momentum, thus a magnetic moment. When a constant magnetic field is applied, a nucleus will resonate like a mechanical oscillator when driven in to an excited energy state by an EM wave (in the radio frequency for NMR) at the correct frequency, which is determined by the strength of the magnetic field and the magnetic moment of the nucleus. Traditionally, NMR was done by sweeping the magnetic field strength while applying a continuous EM wave and measuring where the signal from the nuclei emitted peaked (continuous wave NMR, or CW NMR). However, modern NMR is usually done by applying a pulse of RF waves (pulsed NMR), which contains a broad spectrum of frequency components, and then measuring the resulting radio signal emitted from the nuclei after the pulse. This signal is termed the free induction decay (FID) as it decays similar a damped oscillator. However, modern NMR is usually done by applying a pulse of RF wave (pulsed NMR), which contains a broad spectrum of frequency components, and measuring the radio signal, termed the free induction decay (FID) as the signal decays like a damped oscillator, emitted from the nuclei after the pulse. Using a Fourier transform of the FID signal, the resonance frequency of the nuclei can be determined.

Moreover, pulsed NMR can provide information concerning the physical properties of the nuclei measured. One of the properties is the relaxation times, or the time required for the nuclei in the sample to return to their ground state after being saturated by a strong EM pulse, of the sample. In this experiment, we attempt to measure the relaxation times of acetone, using proton NMR, with various concentrations of gadolinium added as well as glycerol, which will serve as a standard to compare our results to measurements from other experiments. In this experiment, we attempt to measure, using proton NMR, the relaxation times of acetone with various concentrations of gadolinium added, as well as glycerol, which will serve as a standard by which to compare our results to measurements from other experiments.

2 Theory of Experiment

For a formal and comprehensive treatment on the theory of NMR and relaxation times, please refer to a textbook on the subject of NMR spectroscopy [1]. This section will instead focus primarily on the theory directly relevant to our experiment.

2.1 Measuring T_1

To measure T_1 , the spin-lattice relaxation time, a 90° pulse is first applied to the sample so that the z -component of the total magnetization vector is rotated onto the xy -plane, which induces a FID. Then another 90° pulse is applied after a certain time τ to again rotate the magnetization that decayed back to the z -axis into the xy -plane, where the precession of the magnetic moment becomes measurable. The 90° pulse can be repeated in series to obtain a clearer signal through averaging.

Mathematically, this process can be described by a simplified version of the Bloch equations in the z -component [2]:

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1}$$

This first-order differential equation has a solution of:

$$M_z(\tau) = M_0 (1 - e^{-\tau/T_1})$$

Linearizing this equation gives:

$$\ln \left(1 - \frac{M_z(\tau)}{M_0} \right) = -\frac{\tau}{T_1}$$

M_z is directly related to the signal strength of the FID, and M_0 can be measured from the FID by applying a 90° pulse after allowing the sample to settle for several seconds. Therefore, by plotting $\ln \left(1 - \frac{M_z(\tau)}{M_0} \right)$ versus τ , T_1 can be derived from the slope of the linear fitting function.

2.2 Measuring T_2

In theory, T_2 can be measured by examining the envelope of the FID directly. However, inhomogeneity in the magnetic field applied causes the individual magnetic moments of the nuclei to precess at slightly different frequencies and de-phase, where they will begin to partially cancel each other, as the signal decays. This will reduce the component of the total magnetization vector in the xy -plane faster than by T_2 alone. This effective decay time is termed T_2 inhomogeneous and is always less than the pure T_2 . To solve this problem, a 180° pulse is applied after a time τ after the initial 90° pulse. This reverses the phase of the individual magnetic moments of the nuclei so that the higher frequency moments now lag the lower frequency ones and vice versa. After a time τ following the 180° pulse, the magnetic moments will be in-phase again and generate a signal, a spin echo, whose strength depends solely on the pure T_2 and the time that has elapsed since the 90° pulse (2τ).

Mathematically, this process can also be described using a simplified version of the Bloch equations in the transverse direction [2]:

$$\frac{dM_{xy}}{dt} = -\frac{M_{xy}}{T_2}$$

This equation has a solution of:

$$M_{xy}(\tau) = M_{xy0} (e^{-\tau/T_2})$$

Linearizing this equation gives:

$$\ln \left(\frac{M_{xy}(\tau)}{M_{xy0}} \right) = \ln (M_{xy}(\tau)) - \ln (M_{xy0}) = -\frac{\tau}{T_2}$$

By plotting $\ln (M_{xy}(2\tau))$ versus 2τ , T_2 can be obtained from the slope of the linear fitting function.

2.3 Effects of Gadolinium on Relaxation Times

The longitudinal relaxation process (T_1), termed the spin-lattice relaxation, is determined by the time required for an excited proton in a molecule to transfer its spin angular momentum to other materials in its environment. Gadolinium, having 7 unpaired electrons in its highest f orbital, is a paramagnetic atom that provides a route to quickly allow the protons to transfer their spin angular momentum. Thus, adding a gadolinium compound into a solution is expected to decrease the T_1 of the solution. On the other hand, the transverse relaxation process (T_2), termed the spin-spin relaxation, is determined by the time needed for excited protons in a molecule to transfer their spin angular momentum to each other. Since this entirely an intra-molecular process, addition of gadolinium into the solution should have little or no effect on T_2 .

3 Results

3.1 Experimental Setup

The sample is placed in a glass test tube and secured in a sample holder between two Helmholtz coils where the magnetic field generated by the coils is relatively homogeneous. The Helmholtz coils are powered by a DC power supply with a voltage of approximately 35V and a current of 2.6A (the current was adjusted to obtain the optimal signal when the samples were pulsed). Inside the sample holder, there is a set of coil for transmitting the pulsed RF wave used to excite the sample and another set of coil to receive the signal emanating from the sample. The two signal coils are arranged perpendicular to the magnetic field generated by the Helmholtz coils and to each other.

Figure 1 illustrates how the different components of the experimental apparatus are connected. A computer running LabView generates an electric pulse (5V) used to gate the signal from an RF signal generator set at 8MHz (8MHz is approximately the resonance frequency of protons in a 1T field). The gate is opened during the pulse and sends the 8MHz RF pulse through an amplifier to the transmitting coil sample. After the pulse, the signal from the sample is received through the receiver coil and sent to a demixer. The demixer filters out the artifact signals generated by the strong RF pulse and prevents those

signals from saturating out the signals from the samples. The phase shifter corrects the for the phase difference caused by the two signal paths from the RF generator having different path lengths. The final signal is then viewed on an oscilloscope. The gating signal is also connected to the oscilloscope for triggering purposes.

3.2 Measurements for T_1

To determine T_1 , M_z , which is directly proportional to signal strength in volts, at several different τ 's were measured. Figure 2, using data for pure acetone recorded directly from the oscilloscope, demonstrates how these measurements were done on the oscilloscope. To recover a clean signal, signals from 32 90° pulses with the same τ were averaged together. The difference in voltage between the first two extrema clearly identifiable as parts of the FID signal was recorded (between the two horizontal red lines under the arrows in Figure 2).

After a set of measurements (usually ten data points) for a sample had been obtained, the M_0 for that sample was measured using a similar technique, although the signal in this case was not averaged. The points were then plotted and a least-square linear fitting was done to them, as demonstrated in Figure 3.

The values for T_1 derived from repeating the above steps for all the samples are: 12.8 ± 9 ms for glycerol, 247 ± 6 ms for pure acetone, 69.0 ± 6.2 ms for 5ml acetone with 0.01g Gd added, 52.4 ± 4.2 ms for 5ml acetone with 0.05g Gd added, and 10.5 ± 0.6 ms for 5ml acetone with 0.1g Gd added.

3.3 Measurements for T_2

To obtain T_2 , the screen of the oscilloscope was centered to a time 2τ after the initial 90° pulse (or τ after the 180° pulse) for each measurement. The strength of the spin echo was then measured as illustrated in Figure 4. The voltage difference between the central peak and the peak that gave the largest voltage difference of the two that surrounded it was recorded as $M_{xy}(2\tau)$ (between the two horizontal red lines under the arrows in Figure 4). After such a set of M_{xy} at different 2τ 's was obtained from a sample, the points were then plotted and a least-square linear fitting was done as in Figure 5.

The values for T_2 obtained from repeating the above steps for all the samples are: 10.7 ± 0.4 ms for glycerol, 13.2 ± 1.4 ms for pure acetone, 10.6 ± 0.3 ms for 5ml acetone with 0.01g Gd added, 9.40 ± 0.43 ms for 5ml acetone with 0.05g Gd added, and 9.68 ± 0.73 ms for 5ml acetone with 0.1g Gd added.

4 Discussions

The T_1 and T_2 values obtained during this experiment are summarized in Table 1.

Compared to two other reports that reported relaxation times for glycerol [3, 6], our T_1 and T_2 appear to be in general agreement (within a factor of 2) with the values reported

in those reports. Unfortunately, no published materials containing the relaxation time of glycerol were found. Therefore, it may be difficult to determine the accuracy of our calculated relaxation times.

For acetone, T_1 decreased as more Gd was added; this result agrees with the expectation that adding a paramagnetic material will shorten the spin-lattice relaxation time. Between 0.05g and 0.1g of Gd, there is a sharp drop (by a factor of 5) in T_1 when Gd concentration is doubled, suggesting there may be a critical concentration of Gd when a dramatic drop in T_1 occurs. Nevertheless, until the T_1 of more concentrations can be determined, the preceding proposal remains highly uncertain.

T_2 for acetone remained relatively constant throughout the entire Gd concentration range tested. This agrees well with the prediction that spin-spin relaxation is not significantly affected by the proton's external environment.

In conclusion, the results obtained in this experiment appear to be in good agreement with the expected outcomes. Nevertheless, as we are unable to locate published relaxation times for acetone and glycerol, our experiment should be regarded as only a moderate success.

5 Materials and Methods

5.1 Sample Preparation

The glycerol and acetone used were taken from the general chemical stock in the Physics 173 lab at the University of California, San Diego. For each sample, 5ml of the desired sample was pipetted from the stock solution into a 15ml glass test tube. The gadolinium compound used was purchased from Sigma-Aldrich and the name of the product is Resolve-AlTM Gd (chemical formula $\text{Gd}(\text{OCC}(\text{CH}_3)_3\text{CHCO}(\text{CH}_3)_3)_3$, CAS number 14768-15-1). The Gd compound was weighted using an electronic balance and added to the acetone in the sample test tube. The solution was then lightly vortexed to dissolve the Gd compound. The prepared samples were then placed into the sample holder in the NMR machine and measurements were taken.

5.2 Oscilloscope Data

The oscilloscope used, a Tektronix TDS3034B, allows waveforms displayed on its screen to be stored to a disk. The format chosen to store the waveforms is a standard CSV (comma separated values) file format. Microsoft Excel was used to plot the stored data.

5.3 LabView Configuration and Pulse Generation

For measuring T_1 , a single counter under the control of LabView, with adjustable pulse width and delay, was used to generate the pulse. To generate a spin echo, signals from two independent counters, where the first counter gated the second one, were combined through an XOR gate.

The proper duration for a 90° pulse was found by searching for the shortest pulse width where the FID signal from a sample was at a maximum. 180° is two times the width of a 90° pulse.

5.4 Error Propagation

In general, if a value is derived from a function as such: $y = f(x_1, x_2, \dots, x_n)$ and each of the variable of the function, x_i , has an error, assumed to be Gaussian, δx_i , then the error in the final value is [4]:

$$\delta y = \sqrt{\sum_{i=1}^n \left[\left(\frac{\partial f}{\partial x_i} \delta x_i \right)^2 \right]}$$

In the case for T_1 ,

$$y = f(M_z, M_{z0}) = \ln \left(1 - \frac{M_z}{M_{z0}} \right)$$

so

$$\begin{aligned} \delta y &= \sqrt{\left(\frac{\partial f}{\partial M_z} \delta M_z \right)^2 + \left(\frac{\partial f}{\partial M_0} \delta M_0 \right)^2} \\ &= \sqrt{\left(-\frac{M_z}{M_0 - M_z} \delta M_z \right)^2 + \left(\frac{M_z}{M_0 (M_0 - M_z)} \delta M_0 \right)^2} \end{aligned}$$

For T_2 ,

$$y = f(M_{xy}) = \ln(M_{xy})$$

so

$$\delta y = \sqrt{\left(\frac{\partial f}{\partial M_{xy}} \delta M_{xy} \right)^2} = \frac{\delta M_{xy}}{M_{xy}}$$

Since the slope of the linear function, a , used to fit the data for both T_1 and T_2 is the negative inverse of the actual T values, the error in the T values become:

$$\delta T = \frac{\delta a}{a^2}$$

5.5 Linear Fitting

Mathematica 5.2 from Wolfram Research was used to fit the data sets to their best fitting linear functions using the least-squared method. This is done using the Regress function in the Statistics standard add-on package in Mathematica, and the data points were weighted according to the inverse of their variance when calculating the least-square of the fit. Please

refer to the documentation in Mathematica for information on how to use the Regress function [5].

Tables and Figures

<i>Sample</i>	T_1 (ms)	T_2 (ms)
Glycerol	12.8 ± 0.9	10.7 ± 0.4
Acetone	247 ± 6	13.2 ± 1.4
5ml Acetone + 0.01g Gd	69.0 ± 6.2	10.6 ± 0.3
5ml Acetone + 0.05g Gd	52.4 ± 4.2	9.40 ± 0.43
5ml Acetone + 0.1g Gd	10.5 ± 0.6	9.68 ± 0.73

Table 1: T_1 and T_2 for the samples measured.

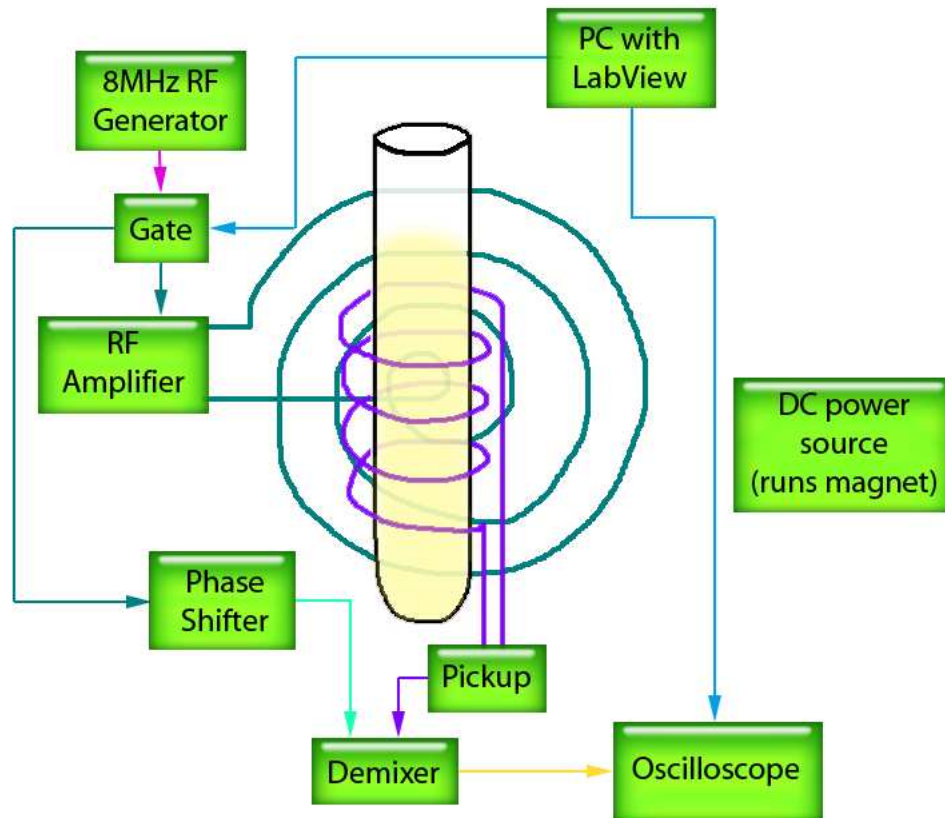


Figure 1: Diagram of experimental setup.

Acetone T1 Measurement

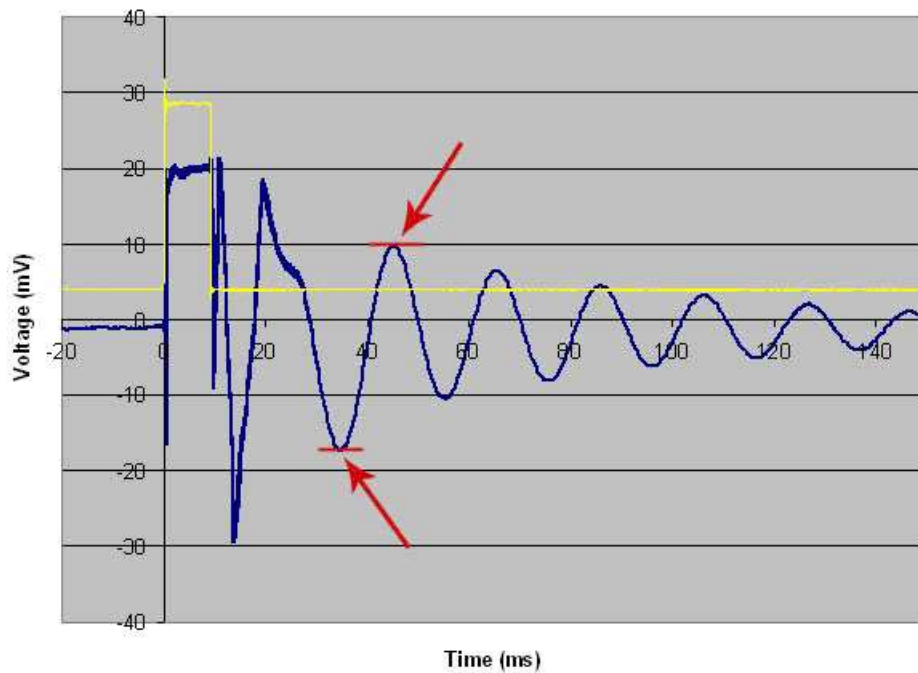


Figure 2: Measuring M_z from a FID. The blue line is the signal from the receiver coil, and the yellow line (not to scale, it is actually 5V in height) is the gating signal from the computer.

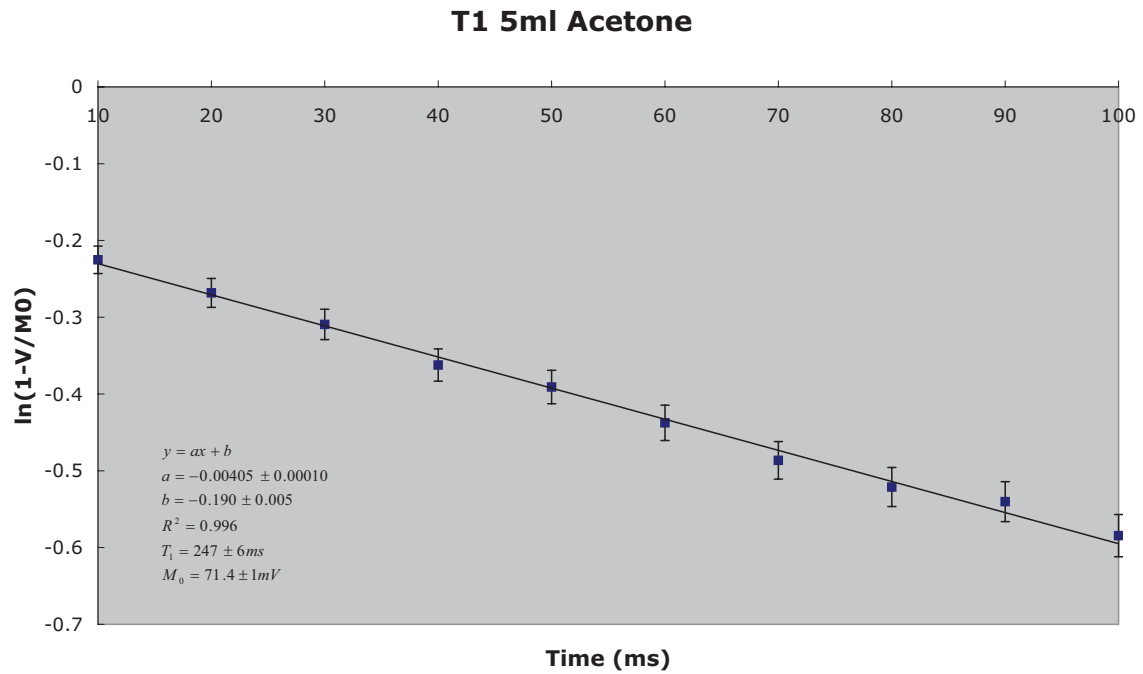


Figure 3: Linear fitting for T1.

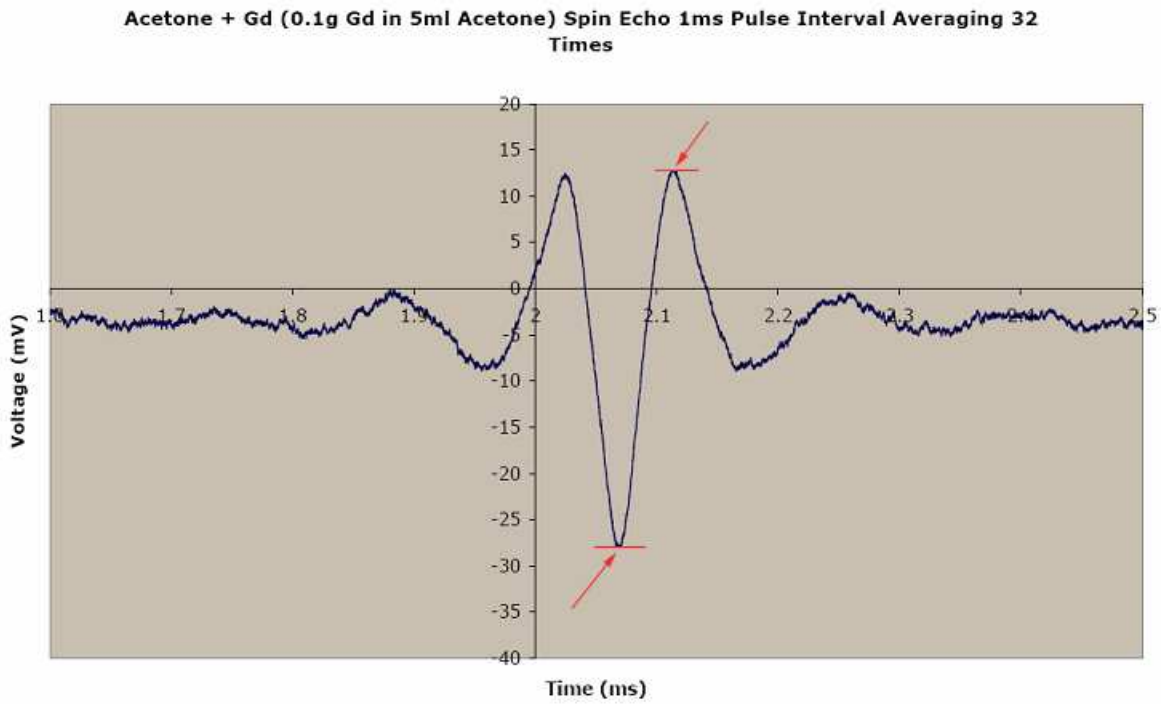


Figure 4: Measuring M_{xy} using a spin echo.

T2 0.05g Gd in 5ml Acetone

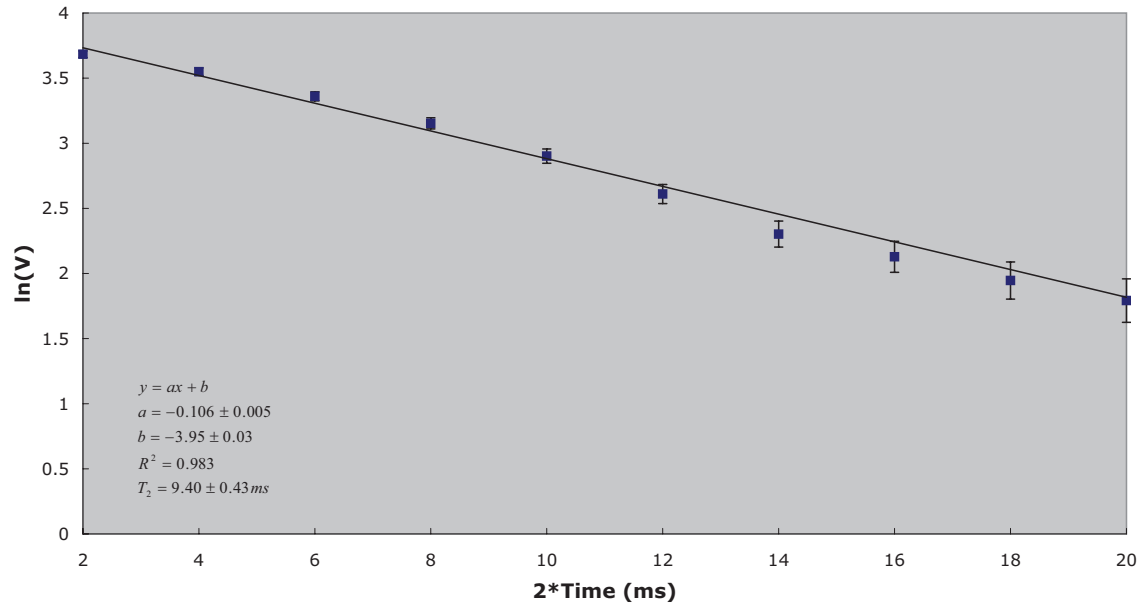


Figure 5: Linear fitting for T_2 .

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