PHYS 403

Lab Report (100 pts) Grading Method

Names_____ Oren Yang and Eric Yu _____

CRITERIA	Eugene	Alexey
Science overview (20)	18	
Procedures (30)	30	
Results / Analysis (30)	30	
Technical quality of the report: graphs, figure captions, tables, references, check spelling etc. (20)	19	
Final Totals (100)	97	98

98

OTHER COMMENTS:

I am sure that you know about this, but you need also to write correctly that you are investigating of the protons (hydrogen nuclear) in different environments glycerol-water solutions). Yes, on page 4 I found the evidence that you know about this but but it should be clear presented starting title of the paper. Also NMR is resonance phenomenom and it should be explained what is the Larmor frequency and how it is linked to magnetic field. Results/analysis - you have got good data and results are presented well too. There are some technical comments (see in text)

What relaxation time you are investigated and why '... of clyserol and Ethanol..." - you were working with NMR of H (protons)?

Relaxation Times of Glycerol in Ethanol Using Pulsed Nuclear Magnetic Resonance

Yes, the title is not very informative.

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Abstract

In nuclear magnetic resonance imaging (MRI), T_1 and T_2 proton relaxation times are used to classify organic tissue. Understanding how these times change in different molecules and mixtures is crucial to improve MRI and to achieve more accurate diagnosis. We use pulsed nuclear magnetic resonance to measure the T_1 and T_2 relaxation times of differing concentrations of glycerin in ethanol, two alcohols with hugely different viscosities that are commonly found in foods. We find that T_1 decreases as viscosity increases for the entire range of concentrations, which agrees with theory. For T_2, we observe the expected decrease with increasing viscosity for the solutions with greater than 50% glycerol. However, for the solutions with greater than 50% ethanol, this trend is not observed. Factors that would have impacted our measurements, as well as steps we took to mitigate error are discussed.

Introduction

Nuclear magnetic resonance (NMR) in solids and liquids was discovered in 1946 by Bloch and Purcell, for which they received the Nobel Prize. Since then, NMR spectroscopy has become a major tool in analytical chemistry and has also been used to study superconductivity. Most notably, NMR imaging–commonly known as MRI–has become an invaluable tool for medical diagnosis [1]. In MRI, organic tissue is categorized by their proton T_1 and T_2 relaxation times, which makes it important to understand how these times change in different molecules and mixtures [10].

NMR arises when a nucleus with a spin, hence also a magnetic moment $\boldsymbol{\mu}$, is placed in a uniform magnetic field **B** (B-field). When there isn't a B-field the spins of the nuclei in a sample point in random directions, resulting in a net magnetization of zero. The addition of a B-field gives rise to the Zeeman effect, which discretizes the spins. For a spin half nuclei, there are two states: a lower energy state where the spin is aligned with the B-field and a higher energy state where the spin is anti-aligned with the B-field (Fig. 1). More nuclei are in the lower energy state, which creates a net magnetization in the direction of the B-field [2]. Most measurements made using NMR consist of first applying a weaker magnetic field at a frequency inversely proportional to the energy gap to flip the states. The very tiny energy gap between the two states allows the use of radio-frequencies, which makes NMR a minimally invasive probe to study materials on the molecular level [3].

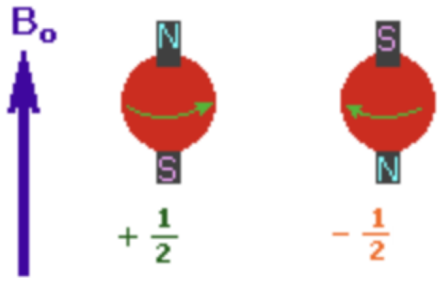

Fig. 1 Spin half nuclei in a uniform B-field. The +½ state is aligned with the B-field and has lower energy. The -½ state is anti-aligned with the B-field and has higher energy [3].

The time derivative of the net magnetization **M** of a sample is described by equation 1. On the right hand side, the first term is the Larmor precession term, which describes a circular precession of the magnetic moment about the direction of the B-field. The frequency of this precession is proportional to the magnitude of the B-field. The second term on the right hand side is the relaxation term we are interested in. Since Larmor precession and relaxation happen on different timescales, and since we will use experimental techniques to bypass the effects of Larmor precession, we set that term to zero. Then, if we choose the positive z-axis to be in the direction of the magnetic field, then the equations describing the bulk magnetization are given by equation 2. T_z is defined to be T_1 and is called the spin-lattice relaxation time. T_x and T_y are equal, defined to be T_2 and is called the spin-spin relaxation time. From a starting magnetization induced by an RF pulse, the magnetization relaxes exponentially to be eventually aligned with the B-field in the positive z-direction.

$$\frac{d\mathbf{M}}{dt} = \gamma(\mathbf{M} \times \mathbf{B}) - \left(\frac{M_x}{T_x}\hat{x} + \frac{M_y}{T_y}\hat{y} + \frac{M_z}{T_z}\hat{z}\right) \tag{1}$$

$$M_x(t) = M_0 \exp(-t/T_x), \quad M_y(t) = M_0 \exp(-t/T_y), \quad M_z(t) = M_0(1-2\exp(-t/T_z)) \tag{2}$$

Surprisingly, there is a close connection between the macroscopic notion of viscosity and nuclear relaxation which happens at the molecular level. There is substantial evidence that T_1, spin-lattice relaxation, decreases as viscosity increases. Thermodynamic interaction with the surrounding lattice are the mechanism behind T_1 relaxation. An increase in viscosity, which corresponds to an increase in lattice interactions, which ends up decreasing T_1. The exact nature of the relationship is proposed to be a proportionality between the viscosity and $1/T_1$, but in practice, the relationship is only roughly satisfied in certain viscosity ranges for certain solutions. The spin-spin relaxation time T_2 also decreases monotonically as viscosity increases [4] [5].

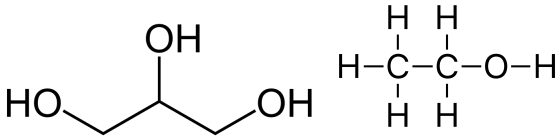

Fig. 2 Glycerol (left) and ethanol (right) are both alcohols that are found in food items. The expensive hydrogen bonding in glycerol makes it very viscous [6] [7].

We study the T_1 and T_2 relaxation times of different concentrations of glycerol in ethanol. Specifically, we are measuring the relaxation times of the hydrogen atoms (protons) in our samples. Both glycerol and ethanol contain these hydrogen atoms, as shown in Fig. 2. Glycerin has a high viscosity (not dissimilar to that of honey) because of the expensive hydrogen bonds in its structure. Ethanol, on the other hand, has a viscosity similar to that of water [6] [7]. Both are found in foods humans consume: glycerin is naturally sweet and is found in many naturally fermented foods such as beer, honey, and vinegar [8], and ethanol is 'the alcohol' in alcoholic beverages. Because they are parts of the diets of many humans, understanding the quantitative behavior of T_1 and T_2 is important to better understanding of how glycerol and ethanol interact with our bodies when using NMR imaging.

Procedure

The first step in this experiment is to create the samples that will be measured. For this experiment, the samples used were glycerin and ethanol solutions ranging from 100% glycerin to 100% ethanol in 5% increments by weight. To create these samples, glycerin was added to a beaker and weighed, and then ethanol was added to achieve the desired concentrations. The solution was then pipetted into small test tubes to be analyzed in the NMR device. Over the course of the lab, multiple samples of some concentrations were made to confirm proper procedures were followed and that the concentrations were reliable.

With the samples created, we began the data acquisition by loading a sample into the TeachSpin PS1-A pulsed nuclear magnetic spectrometer. Figure 3 shows an image of the sample loaded into the device along with a schematic of the internal configuration of the device. Permanent magnets are located on either side of the device to align the spin in the sample, and then an RF pulse can be applied to adjust the orientation of the spin. There is also a coil around the sample used to measure the component of the spin in the vertical direction. The device is connected to an RF source, and is both controlled by and outputs the measured data to a computer. A schematic of the full set up is depicted in figure 4.

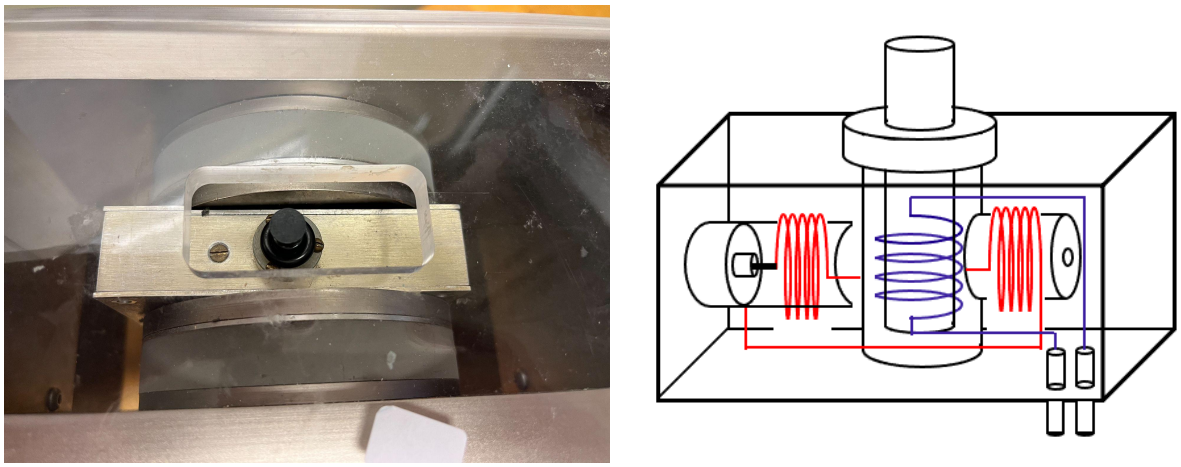

Fig. 3 Photograph of sample in TeachSpin spectrometer (left) and schematic of coils in the spectrometer (right).

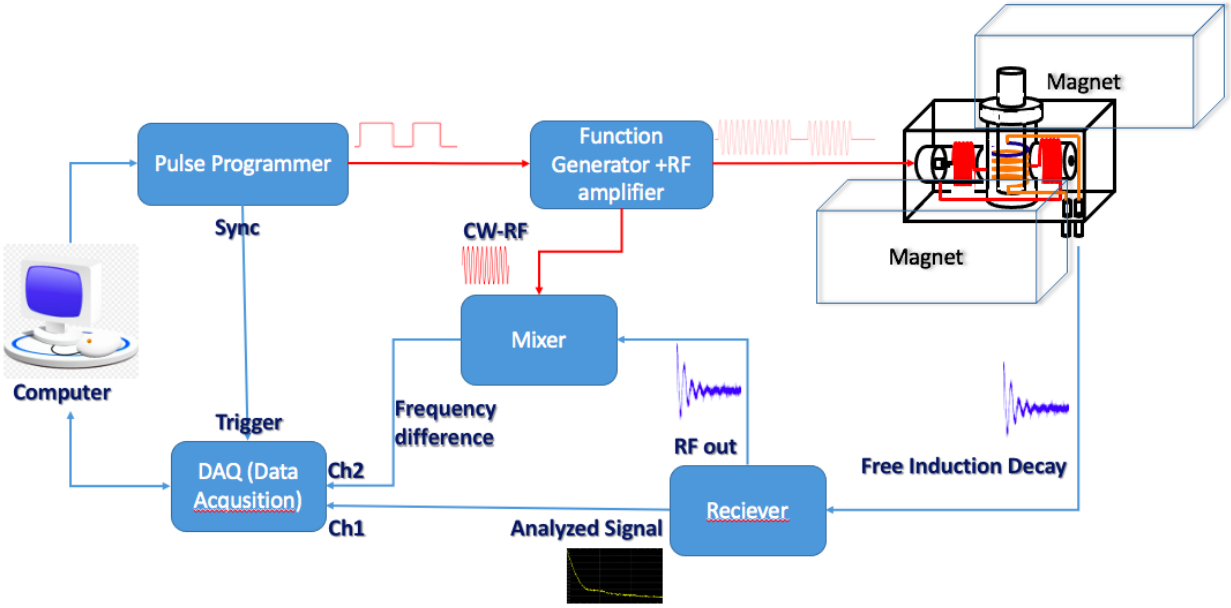

Fig. 4 Schematic of PNMR setup including the radio-frequency system, TeachSpin spectrometer, and data acquisition systems.

To gather data, the RF supply must first be tuned corresponding to the Larmor precession of the magnetic moment in the sample. Next, the RF pulse is calibrated to accurately orient the spin in the correct direction. The provided NMR software allows one to check the quality of the tuning and easily calibrate the pulse.

The software is then used to record data for the T_1 and T_2 times by adjusting the direction of the spin to different angles and measuring the vertical component of the spin at some delay time

after the pulse, as the spin relaxes to match the permanent magnets. The full scan for one sample involves increasing the delay time from zero seconds until the shape of the detector maximum versus delay time plot approaches a constant value, meaning that the delay time is so long that the sample has fully relaxed before being measured.

As the sample sits in the device, it will slowly get out of tune with the RF source, so there are two major parameters to adjust while taking these measurements to ensure that the data is accurate and recorded quick enough to keep the system in tune; repetition time and step size. The repetition time is the time between measurements of different delay times. This is important because if the repetition time is shorter than the time for the sample to fully relax, then following measurements will not be accurate. Because the system detunes over time, if the repetition time needs to be increased, the step size must be increased accordingly so that the full measurement can finish before detuning. The step size determines how much the delay time changes between each data point. The pulse sequence of a T_2 measurement is shown in figure 5. In this figure, the RF pulses and the degree to which they rotate the spin is shown by the green curve. The 't' under the green curve describes the delay time. The measurement is taken during the echo, twice the delay time after the first pulse.

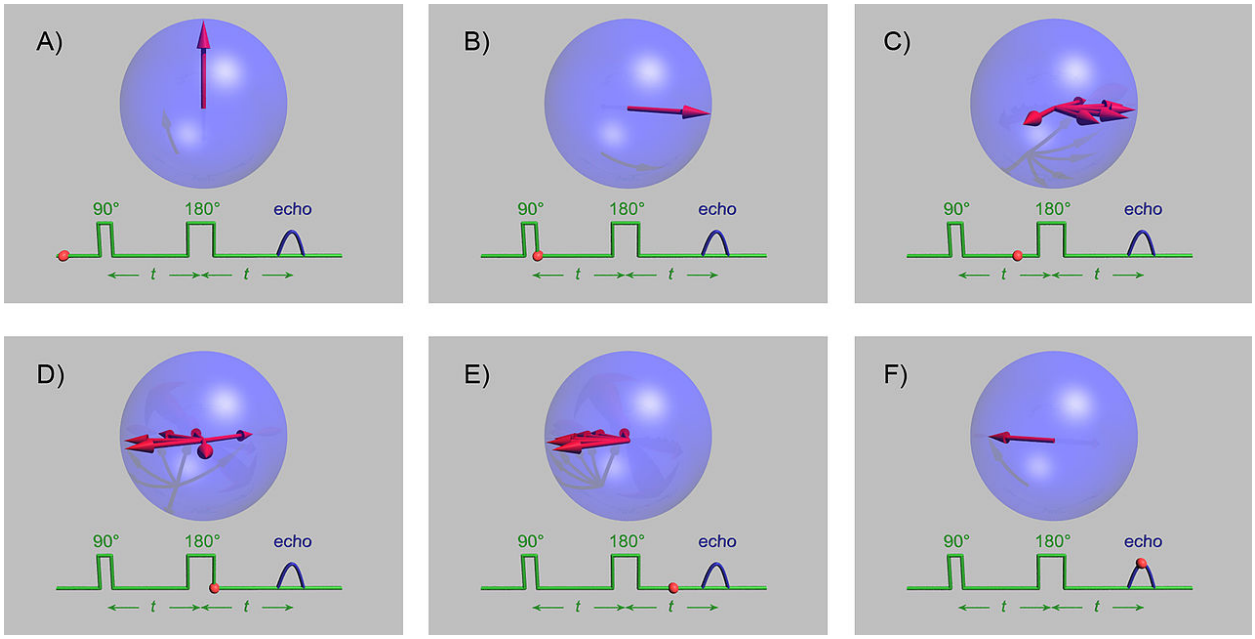

Fig. 5 Step by step process of the spin echo and the pulse sequence used for measuring spin-spin relaxation times [11].

Results & Analysis

After the measurements are complete, the raw data is fitted to exponential decay functions to determine the T_1 and T_2 values. An example of the fits to T_1 and T_2 are included in figure 6. The

exponential decay function used for the fit is shown by equation 3, where T_R is the spin-spin or spin-lattice relaxation time and A and y_0 are constants.

$$y = Ae^{-x/T_R} + y_0 \tag{3}$$

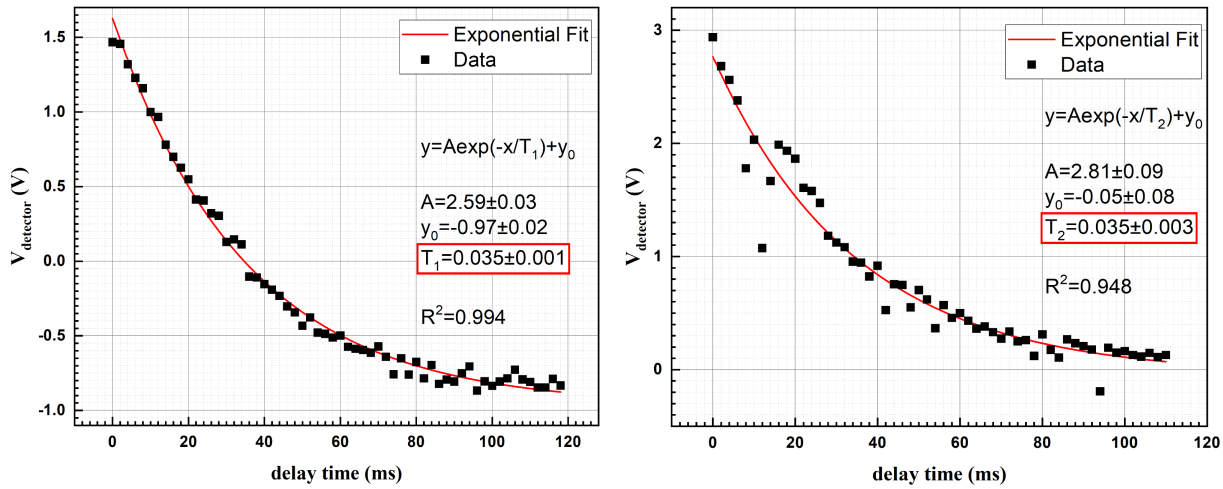

Fig. 6 Exponential fitting of the raw detector maximum versus delay time data for T_1 (left) and T_2 (right). All fitting was done in Origin.

what sample was used in this experiment?

For T_1, all of the samples gave results that closely matched the exponential decay shape, giving high r^2 values around 0.99, and relatively low error on the calculated values for T_1. T_2 gave less reliable results and many samples had to be repeated multiple times with slight variations in repetition time and step size in order to achieve accurate data. In the end, we were able to find improved conditions for T_2 to get an r^2 around 0.9 for all of the samples.

Once all the samples were fitted, we plotted T_1 and T_2 against concentration of glycerin in ethanol to find the trend of the relaxation times. The results for T_1 are presented in figure 7, and T_2 in figure 8. Figure 7 shows that as the mixture goes from 100% glycerol to 100% ethanol, the spin-lattice relaxation time increases significantly from less than 0.05 seconds to almost 1 second. This result is in agreement with expectations based on theory, which state that the spin-lattice relaxation time should decrease with increasing viscosity.

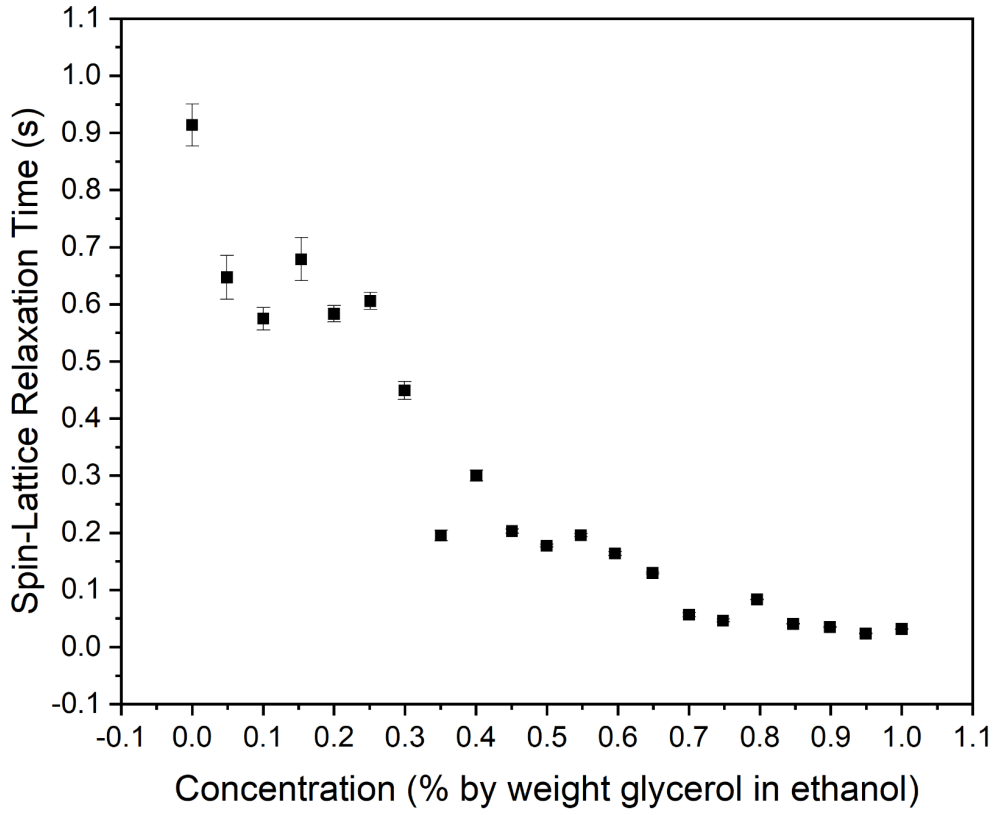

Fig 7. Plot of the spin-lattice relaxation times, T_1, versus the weight percent of glycerol in ethanol.

The results of the spin-spin relaxation time are shown in figure 8 and, similar to T_1, show the trend of increasing relaxation time. In this case, however, as the glycerol concentration continues to decrease below 50% by weight, that trend is no longer observed. The change in trend seemingly disagrees with the theory, however a similar change in trend was seen by Kim (2008) as shown in figure 9, where at a certain viscosity, the T_2 relaxation time seemed to hit a maximum and stop increasing as viscosity continued to decrease [9].

what theory?

I do not see the maximum in T2 vs concentration dependence (looks more like it saturates at los concentration) and it is it water glycerol solution

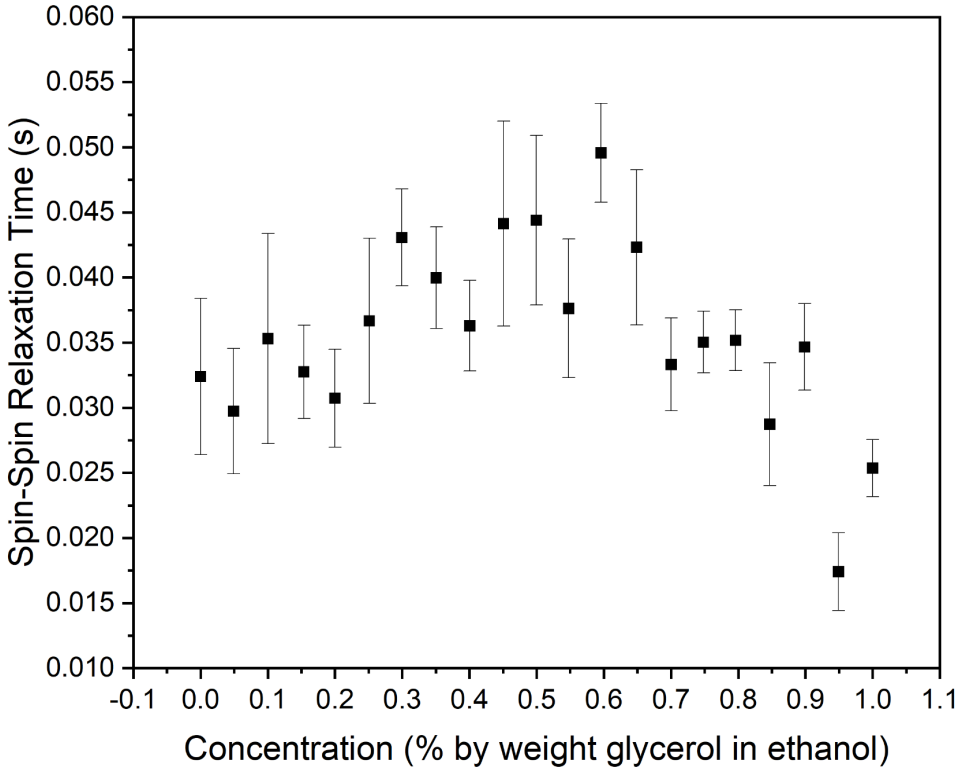

Fig. 8 Plot of the spin-spin relaxation times, T_2, versus the weight percent of glycerol in ethanol.

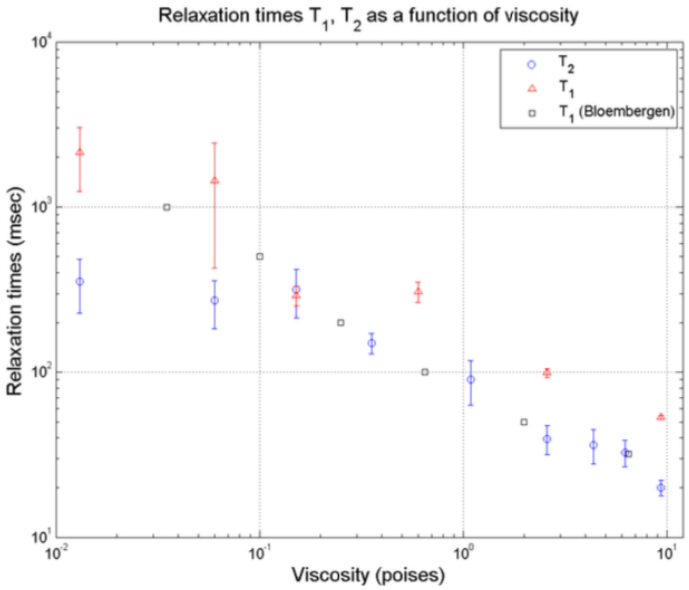

Fig. 9 Relaxation times plotted as a function of viscosity. Data was measured using glycerin-water solutions [9].

Throughout the experiment, actions were taken to mitigate error wherever possible. Multiple samples were remade and remeasured to mitigate error in the actual concentration versus the recorded concentration. Additional error sources arose as the viscosity of the samples decreased because the significantly longer relaxation times required much longer repetition times, which in turn led to detuning of the system before the experiments were completed. The process for measuring data was repeated many times for some samples until the optimal conditions were achieved and we had minimized this error as much as possible. Measurement of the T_2 times showed more error than T_1, with the measured detector signal making significant and unexpected jumps instead of following the expected exponential decay trend. These points likely affected our data for T_2 and, while much time was spent optimizing the process to limit this error, the final results were not as clear as the T_1 results. As a result, there are relatively larger error bars on the T_2 data.

Conclusions

The T_1 relaxation time of the glycerol-ethanol samples we studied exhibit expected behavior of monotonically decreasing as viscosity increases for the entire concentration range. The T_2 relaxation time, however, only exhibits expected behavior in the more viscous part of the concentration range, where the solution has more glycerol than ethanol.

References

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link:https://commons.wikimedia.org/wiki/File:SpinEcho_GWM_stills.jpg