Proton Relaxation in Aqueous Fe^{+3} Solutions

Jim Gibson
Gates and Crellin Laboratories
California Institute of Technology
May 27, 1966

1. Introduction

The relaxation time of water protons in an externally applied magnetic field is about 3 sec. The addition of paramagnetic ions decreases the relaxation time markedly, as was first shown by Bloch, Hansen, and Packard.[1] This effect was explained by Bloembergen, Purcell, and Pound[2] in terms similar to the nuclear-dipole relaxation interaction, and they derived for T_1 (the transverse, longitudinal, or spin-lattice relaxation time) the formula

$$\frac{1}{T_1} = \frac{12\pi^2\gamma^2\eta N_{ion}\mu_{eff}^2}{5kT}$$

where γ = gyromagnetic ratio of proton

η = viscosity of solution

N_{ion} = concentration of paramagnetic ion

μ_{eff} = magnetic moment of ion

This present work investigated the dependence of T_1 upon the concentration of the paramagnetic ion for very low concentrations using aqueous Fe^{+3} solutions. The solutions were degassed using a freeze-thaw technique to remove dissolved oxygen which is also paramagnetic. The method used for measuring T_1 was the spin-echo method of Hahn[3] using a pulse sequence described by Carr and Purcell.[4]

2. Theory

Let $\overline{M}$ be the total magnetic moment per unit volume of an ensemble of nuclei with gyromagnetic ratio γ. The differential equation governing the relaxation of

the spins is

$$\frac{d\bar{M}}{dt} = (\bar{M} \times \bar{H}) - \bar{I}\frac{M_x}{T_2} - \bar{J}\frac{M_y}{T_2} - \bar{k}\frac{(M_z - M_o)}{T_1}$$

$$\text{with } \bar{H}(t) = \bar{k}H_o + \bar{H}_1(t)$$

Thus, in the absence of $H_1(t)$, M_z will approach the value M_o with a characteristic time constant T_1, the longitudinal relaxation time. If $\bar{M}$ makes an angle with $\bar{H}$, it will precess about $\bar{H}$ with a frequency $-\gamma|\bar{H}|$. If a rotating magnetic field of frequency $\omega = -\gamma|\bar{H}|$ is applied, it will cause the magnetic moment to nutate about this field away from the direction of the field $\bar{k}H_o$ in the z-direction towards the xy-plane.

Viewed from a coordinate system which is rotating with a frequency just equal to the frequency of precession of $\bar{M}$, the magnetic moment vector $\bar{M}$ appears to be stationary. When the rotating magnetic field $\bar{H}_1(t)$ is applied, it also appears stationary and the magnetic moment $\bar{M}$ precesses about it through an angle $\gamma H_1 t$ in a time t. If the field $\bar{H}_1(t)$ is applied along the x'-axis in the rotating coordinate system for a time t_{90} such that $H_1 t_{90} = \frac{\pi}{2}$, then $\bar{M}$ will be rotated from the z-axis through an angle of 90° to the y'-axis in the rotating coordinate system. The application of H_1 for a time t_{90} is a "90° pulse." In a time $t_{180} = 2t_{90}$, the magnetic moment $\bar{M}$ will have been rotated through an angle of 180° to the -z-axis. This is a "180° pulse."

In the present experiments, T_1 was measured using a 180° pulse followed at a later time by a 90° pulse.

The 180° pulse reverses the direction of the magnetization from the +z to the-z direction. Then the spins begin to relax and the z component of $\bar{M}$ changes from $-M_0$ to $+M_0$ with a characteristic time constant T_1, i.e.

$$M_z(t) = -M_0(2e^{-t/T_1} - 1)$$

At varying times during this process, a 90° pulse is applied. This rotates the partially relaxed magnetic moment from along the z-axis into the xy-plane where it can be detected in the reciever coil. The strength of the signal depends upon the magnitude of $\bar{M}$ when the 90° pulse was applied. If it applied soom after the 180° pulse, then the magnetic moment $\bar{M}$ will not have relaxed a great deal and the signal will be close to maximum amplitude. If it is applied long after, then $\bar{M}$ will have relaxed back to maximum magnitude in the +z direction and the signal will also be strong. The time for which the magnitude of $M_z = 0$ and for which no signal results upon application of a 90° pulse is called τ_{null} and is given by $\tau_{null} = T_1 \ln 2$. In the present experiments, the 90° pulse was shifted to the point in time of minimum signal from the reciever coil and the time interval between the pulses measured for τ_{null}, and T_1 was computed.

The effect of the addition of paramagnetic ions on the relaxation times of the protons is that of two seperate processes, the electron-nuclear dipole-dipole interaction and the scalar coupling or spin-exchange interaction. The spin-exchange interaction is present to a significant degree in only certain cases, such as Mn^{++} solutions[4], in which the T_1/T_2 ratio is larger than that predicted

by the dipolar interaction alone. In the case of most paramagnetic ions, the electron relaxation time of the ion is too short to allow any interaction with the protons, and the ratio T_1/T_2 is about unity with $1/T_1$ and $1/T_2$ having a linear dependence upon the concentration of the ion.

The contributions of both interactions are given by the Hamiltonians.[6]

$$\mathcal{H}_1 = -(\hbar^2\gamma_I\gamma_s/r^3)\left[3(\vec{I}\cdot\vec{r})(\vec{s}\cdot\vec{r}) - \vec{I}\cdot\vec{s}\right]$$

$$\mathcal{H}_2 = A\,\vec{I}\cdot\vec{S}$$

where S = spin of the ion

I = spin of the proton

The relaxation times are added reciprocally:

$$\frac{1}{T} = \frac{1}{T_{dipole}} + \frac{1}{T_{exchange}}$$

The approxiamate relationships resulting are:

$$\frac{1}{T_1} = \frac{4}{30}\frac{S(S+1)\gamma_I^2 g^2\beta^2 p}{r^6}\left[3\tau_c + \frac{7\tau_c}{1+\omega_s^2\tau_c^2}\right] + \frac{2}{3}\frac{S(S+1)A^2 p}{\hbar^2}\left[\frac{\tau_e}{1+\omega_s^2\tau_e^2}\right]$$

$$\frac{1}{T_2} = \frac{4}{60}\frac{S(S+1)\gamma_I^2 g^2\beta^2 p}{r^6}\left[7\tau_c + \frac{13\tau_c}{1+\omega_s^2\tau_c^2}\right] + \frac{1}{3}\frac{S(S+1)A^2 p}{\hbar^2}\left[\frac{\tau_e}{1+\omega_s^2\tau_c^2} + \tau_e\right]$$

where τ_c = correlation time for the dipolar interaction

τ_e = correlation time for the exchange interaction

A = coupling constant for the exchange interaction

p = probability of finding a given proton in the hydration sphere of a paramagnetic ion and is proportional to the ionic concentration

τ_c will have an exponential temperature dependence:

$$\tau_c = \tau_c^{\circ}\exp(V_c/RT)$$

where V_c is the activation energy for the molecular motion of the hydrated ion. τ_c will depend in general upon the electron relaxation time of the paramagnetic ion, τ_s, and upon the correlation time for proton chemical

exchange as well. Either process, a change in the quantization of the electron spin or the chemical exchange of the electron spin or water molecule, can disrupt the scalar coupling between the electron and proton magnetic moments. Whichever process is faster will govern the correlation time for the exchange reaction.

3. Preperation of Solutions

The Fe^{+3} solutions were made up by dissolving reagent grade ironwwire in concentrated nitric acid, boiling off the NO produced, adding H_2O_2 to oxidize any Fe(II) to Fe(III), and boiling off excess H_2O_2 as O_2. These solutions were slowly immersed in liquid nitrogen; then the air above the frozen solutions was pumped out to about .005 mmHg.; the solutions were warmed and allowed to melt. This procedure was repeated at least three times for each sample and four times for the lower concentration ranges. The tubes containing the samples were then sealed off while still under vacuum at a constriction prepared in the tube beforehand.

4. Measurement of T_1

The spin echo pulse sequence used in these experiments is described above. The experimental apparatus used to generate the pulses and observe the induction signals is shown below schematically in Fig.1.

The sequence is as follows: 1) The ERC generator puts out a square wave which triggers the sawtooth gener-

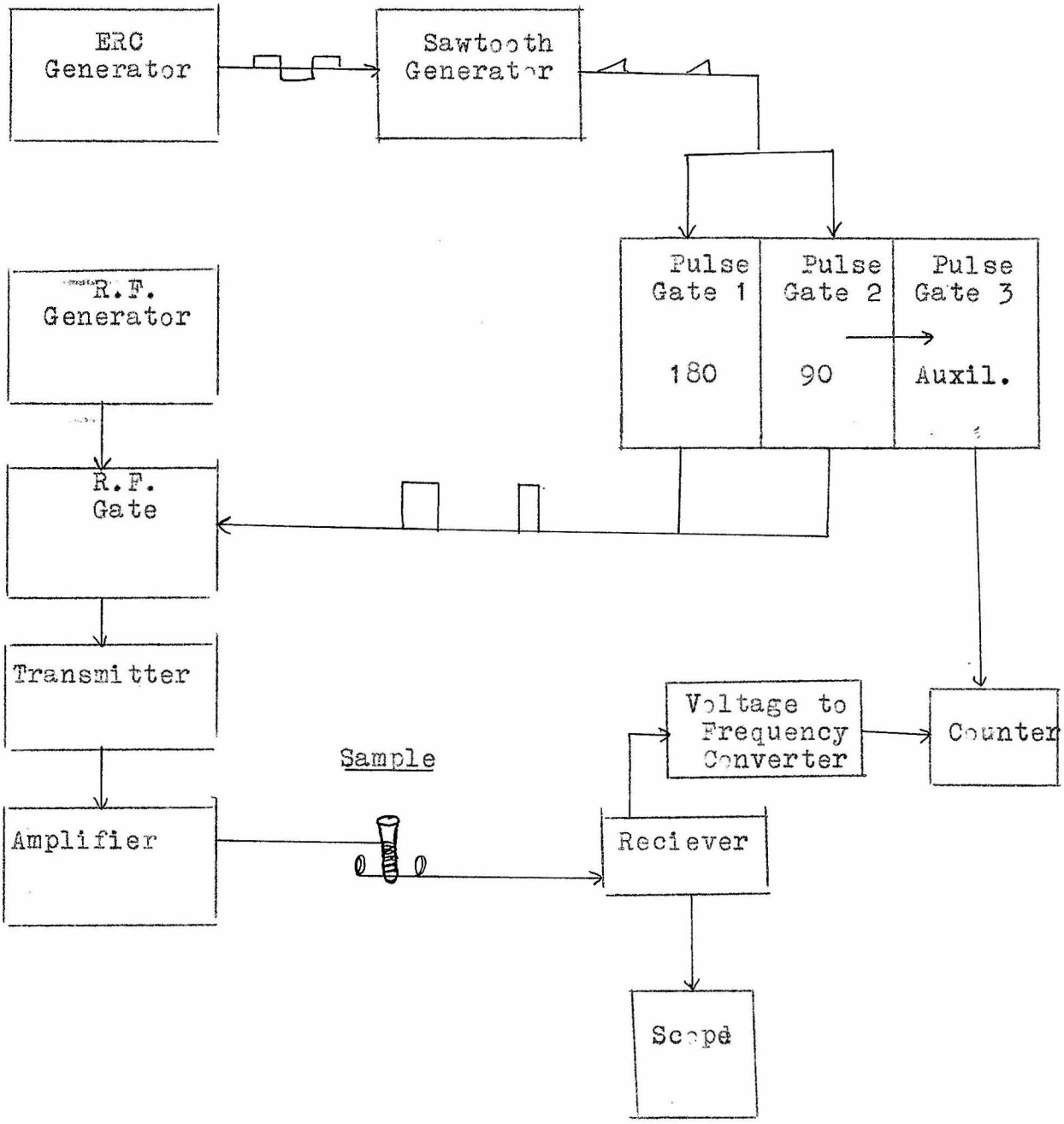

Fig. 1: Pulse NMR device

ator, 2) the sawtooth generator wave triggers the 180 and 90 degree pulse generators with a variable delay, 3) The two pulses open the R.F. gate for their duration which 4) allows the R.F. generator to transmit the RF wave through the transmitter and amplifier to the sample. 5) the induction signal from the sample is the amplified by the reciever and either displayed on the scope or sent to the counter.

From the traces on the scope, τ_{null} can be found by 1) adjusting the delay between the 90 and 180 degree pulses to give zero signal on the scope and observing the position of the spike due to the 90° pulse or 2) by taking a multiple exposure of several sequences with different τ's and observing from the picture where the curve of the maximum peak height envelope cuts the horizontal axis. A more accurate method, however, is by use of the counter. The signal from the sample, in passing through the voltage to frequency converter, is converted from a voltage reading to a proportionate frequency reading. The counter counts the individual beats of the frequency and thereby integrates the signal trace and displays the result in digital form on the counter dials. This integral is set to its minimum value by adjusting τ, the delay between pulses. The counter is then adjusted to measure τ_{null}, the τ setting at the minimum signal point.

The measurement of the T_1's was spread out over a period of two weeks. However, the temperature, which has a proportional effect on T_1, was quite constant at

21-22°C. The pulse widths (or duration) of the 90 and 180 degree pulses were set by visual observation of the signal on the scope. The 90 degree pulse was set for maximum free induction decay signal following the pulse and the 180 degree pulse set for minimum, or zero, free induction decay. Care had to be taken in setting the repitition rate for the pulse sequences. It is necessary to allow the magnetic moment vector $\bar{M}$ to relax completely back to its equilibrium value, $\bar{k}M_0$, before repeating the 180-90 pulse sequence again, or else the moment $\bar{M}$ would start out partially relaxed for the next sequence. For this reason, the frequency of the ERC generator was set to give a period of about $20T_1$ for each sample. This involved rates of 16 to .0167 cycles per second or periods of .06 to 60 seconds per sequence. The RF frequency used was 9 mc. The data for 17 solutions of varying Fe^{+3} concentrations is tabulated in Table 1. The T_1 are plotted versus the log of the Fe^{+3} concentration in Graph 1.

5. Conclusions

From the graph, it can be seen that T_1 is about linear with log(Fe) with slope close to -1, as predicted by Bloembergen, Purcell, and Pound.[2] There does, however, appear to be some indication of two seperate concentration dependences, one above 10^{17} ions/ml. and the other below. This may be the result of the spin-exchange interaction becoming significant at very low ion concentrations.

The experimental values of T_1 were reproducible to

within 3%. The errors in concentrations probably contributed another 1% to the final error.

Table 1: T_1 for Fe^{+3} solutions. 9 mc. 21°C.

Fe^{+3} conc. ions/ml.	null msec.	T_1 sec.	$\log_{10}(Fe^{+3})$
1.08×10^{19}	2.23	3.22×10^{-3}	19.033
6.4×10^{18}	3.93	5.67×10^{-3}	18.806
4.07 "	5,90	8.52×10^{-3}	18.610
2.03 "	11.99	1.73×10^{-2}	18.307
1.12 "	20.93	3.02×10^{-2}	18.049
7.09×10^{17}	34.37	4.96×10^{-2}	17.851
2.82 "	84.17	1.21×10^{-1}	17.450
1.60 "	299.6	4.32×10^{-1}	17.204
1.01 "	300.1	4.33×10^{-1}	17.004
8.04×10^{16}	618.9	8.94×10^{-1}	16.905
3.00 "	890.8	1.29 sec.	16.477
1.5 "	1253	1.81	16.176
1.01 "	1613	2.33	16.004
4.97×10^{15}	2089	3.01	15.696
3.00 "	2102	3.03	15.477
1.99 "	2113	3.05	15.299
1.00 "	2117	3.06	15.000

Bibliography

1. Bloch, Hansen, and Packard; Phys.Rev. 70, 474 (1946)
2. Bloembergen, Purcell, andPound; Phys.Rev. 73, 679 (1948)
3. E.L.Hahn; Phys.Rev. 80, 580 (1950)
4. Carr and Purcell; Phys.Rev. 94, 630 (1954)
5. Bernheim, Brown, Gutowsky, and Woessner; J.Chem.Phys. 30, 950 (1959)

Graph 1: T_1 v. $\log_{10}[Fe^{+3}]$