

DYNAMIC POLARIZATION OF PROTONS IN $\text{NO}(\text{SO}_3)_2^{2-}$ AQUEOUS SOLUTION

BY

Ryoichi KADO

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ABSTRACT

The Overhauser effect in $\text{NO}(\text{SO}_3)_2^{2-}$ aqueous solution was observed at 38 and 3400 gauss. The proton NMR signal was largely enhanced and this enhancement enabled us to perform the low field relaxation measurement otherwise very difficult. Although we could not obtain the value of enhancement factor, the linear dependence of the inverse signal intensity upon the inverse ESR power was confirmed. The proton spin-lattice relaxation time T_1 and the proton polarization time T_p were measured for various concentrations of $\text{NO}(\text{SO}_3)_2^{2-}$ ion by a pulsed NMR method at 38 gauss and by a modified steady-state NMR method utilizing transient signal at 3400 gauss. In addition, the measurement of T_1 was performed at 2350 gauss by a pulsed NMR method. The observed value of T_1 at 2350 and 3400 gauss is about two times that of T_1 at 38 gauss. This fact shows that the condition of "extreme narrowing" is not satisfied at 2350 and 3400 gauss. The calculation of the correlation time τ_c based on the rotational model of random molecular motion yielded 5.6×10^{-11} sec. Using the obtained value of τ_c , the reduced enhancement factor at the high field was evaluated. At 38 gauss T_p was found to be longer than T_1 and to slightly deviate from the exponential curve, whereas they have equal values at 3400 gauss. This effect could be explained qualitatively by the decoupling of proton spins and electron spins due to stirring of electron spins by strong ESR power. No quantitative theory is given up to the present, however, to support this model.

I. Introduction

In 1953 Overhauser predicted the possibility of dynamic nuclear polarization in metals by saturating conduction electron spin resonance (ESR)¹⁾. Soon after, several authors extended the theory to show that this effect could occur in non-metals as well.²⁾ Generally speaking, the Overhauser effect is expected in a system of two spins I and S , mostly nuclear and electron spins, under the following conditions: 1) the coupling between I and S is a function of time due to random fluctuations such as the motion of conduction electrons in metals and semi-conductors or the Brownian motion of molecules in liquids; 2) the spin-lattice relaxation of I is dominated by its coupling with S while S has its own relaxation mechanism. Carver and Slichter first verified this effect experimentally by observing the enhancement of nuclear magnetic resonance (NMR) signal in metallic lithium and sodium.³⁾ Ever since, many investigations have been done for various materials not only to produce nuclear polarization but to study the nature of the coupling between two unlike spins. Double resonance based on the Overhauser effect enables us to obtain much more informations on both nuclear and electron magnetism than any

single resonance method.

In order to analyze the behavior of the spin system of above-mentioned type, we start by writing the following equation of motion developed by Solomon:⁴⁾

$$\frac{d\langle I_z \rangle}{dt} = -\frac{1}{T_1} [\langle I_z \rangle - I_o + f\rho(\langle S_z \rangle - S_o)], \quad \dots\dots\dots(1)$$

where T_1 is the spin-lattice relaxation time of spins I , $\langle I_z \rangle$ and $\langle S_z \rangle$ are polarizations of respective spins, I_o and S_o are their thermal equilibrium values, f is the leakage factor defined as $f=1-T_1/T_{10}$, with T_{10} , the relaxation time corresponding to the mechanisms other than the coupling with S , and ρ is a dimensionless coefficient depending on the nature of I - S coupling. The steady-state solution of eq. (1) is, letting $d\langle I_z \rangle/dt=0$,

$$\langle I_z \rangle = I_o - f\rho(\langle S_z \rangle - S_o).$$

The enhancement factor A is defined as follows;

$$A = \frac{\langle I_z \rangle - I_o}{I_o} = f\rho \frac{\langle S_z \rangle - S_o}{I_o}. \quad \dots\dots\dots(2)$$

Saturating the resonance of spins S completely, one obtains $\langle S_z \rangle = 0$, so

$$A = f\rho \frac{S_o}{I_o} = f\rho \frac{\gamma_S}{\gamma_I}, \quad \dots\dots\dots(3)$$

where γ_I and γ_S are the gyromagnetic ratios of respective spins. If the I - S coupling is of scalar type, ρ takes the value of -1 . Assuming $f=1$ (no leakage), and I and S are proton and electron spins respectively, one obtains the proton polarization of the same degree as the electron polarization at thermal equilibrium. Then the maximum value of enhancement factor is 660. On the other hand, if the coupling is of dipolar type and the correlation time of the random fluctuation is assumed to be very short ("extreme narrowing"), ρ is $1/2$. So the maximum enhancement is -330 . It must be noted that negative polarization results in this case.

Here, we report a work on dynamic polarization of protons in $\text{NO}(\text{SO}_3)_2^{2-}$ (peroxylamine disulphonate ion) aqueous solution. This substance had been well studied by means of ESR⁵⁻⁷⁾ and nuclear-electron double resonance.⁸⁻¹⁴⁾ ESR and NMR lines have very narrow widths, a suitable situation for simple treatment. Since $\text{NO}(\text{SO}_3)_2^{2-}$ ion has a hyperfine structure due to N^{14} nuclei, as illustrated in Fig. 1, $\langle S_z \rangle$ in eq. (2) can not vanish. If one of the three allowed lines is completely saturated, one obtains $\langle S_z \rangle = (2/3) S_o$. Assuming the proton-electron dipolar coupling and extreme narrowing, the maximum enhancement of -110 is expected. Experimentally, an enhancement of about -50 was observed by Allais at 3300 gauss.⁹⁾

The discrepancy was attributed to the insufficiency of microwave power for complete saturation of ESR. On the other hand, in the low field, the ESR frequency goes down into the

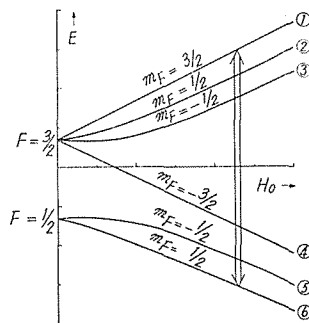


Fig. 1. Energy levels of $\text{NO}(\text{SO}_3)_2^{2-}$ ion derived from the well-known Breit-Rabi formula. The transition between the levels ($F=3/2, m_F=3/2$) and ($F=1/2, m_F=1/2$) was saturated to observe the Overhauser effect.

region of several hundred megacycles and a large rf power is available. Landesman obtained an enhancement of about -100 at 70 gauss.¹⁰⁾ Anyhow, from these experiments, the proton-electron coupling was confirmed to have dipolar origin.

In the course of the present work, we were mainly concerned with the transient behaviors of proton spins in the aqueous solution. Few papers treating this problem were published so far. Müller-Warmuth and his coworkers reported the frequency- and temperature-dependence studies of ρ and T_1 of proton in some organic free radical solutions by means of double resonance technique.^{15,16)} They concluded that the relaxation mechanism could be explained in terms of the translational random motion of molecules. Richards and White made a transient double resonance experiment at a very high field (12500 gauss) on another organic solution.¹⁷⁾ They observed the transient growth and decay of proton polarization and found that these two processes had the same time constants.

We performed double resonance experiments at 38 and 3400 gauss. At 38 gauss, using steady-state method, we studied NMR signal enhancement as a function of ESR power. By means of pulsed double resonance, the proton spin-lattice relaxation time T_1 and the proton polarization time T_p (the time constant associated with the approach of proton spins to the enhanced state) were measured for various concentrations of $\text{NO}(\text{SO}_3)_2^{2-}$ ion. At 3400 gauss, T_1 and T_p were measured by a transient double resonance method. T_1 was also measured at 2350 gauss (proton frequency of 10 Mc/s) by a standard pulsed NMR method. The values of T_1 at three different fields were compared. The correlation time was estimated under the assumption that the random molecular rotation was the dominant relaxation mechanism. A qualitative explanation was attempted for the fact that T_p was longer than T_1 at 38 gauss.

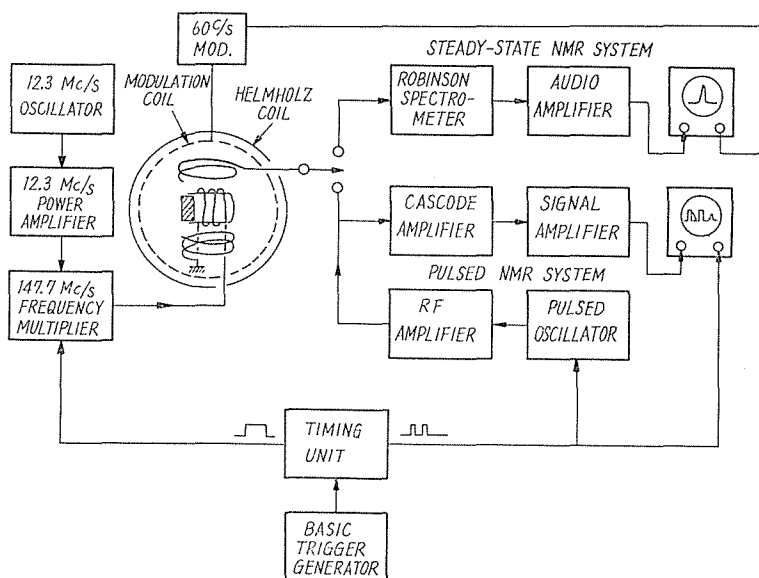


Fig. 2. Block diagram of the double resonance apparatus used in the low field experiment.

II. Experimental Procedure

Experiments were performed on $K_2NO(SO_3)_2$ aqueous solutions of various concentrations at room temperature. Though distilled water was used for solvent, the solutions were not degassed. A small amount of KOH was added in the solution to prevent the decomposition of the ion $NO(SO_3)_2^{2-}$. Since this ion is unstable at high temperature, care was paid to avoid heating due to strong rf power.

(1) Low field experiments

The blockdiagram of the whole apparatus is shown in Fig. 2. A magnetic field of 38 gauss was produced by a Helmholtz coil of 20 cm in diameter. At this field ESR was driven at 147.7 Mc/s, corresponding to the highest frequency transition of $NO(SO_3)_2^{2-}$ ion, as shown in Fig. 1, while the proton NMR frequency was 162 Kc/s.

The ESR system consists of a 12.3 Mc/s oscillator, an amplifier of two stages and a frequency multiplier of three stages. The last two stages of the multiplier have gate tubes to make rf pulses. The circuit diagrams of them are shown in Fig. 3 and 4. The maximum strength of rf field H_{1e} is roughly estimated to be 1.5 gauss. The frequency of the ESR system was measured by a frequency counter. In order to adjust the frequency of the ESR system to be on resonance, a simple spectrometer shown in Fig. 5 was employed.

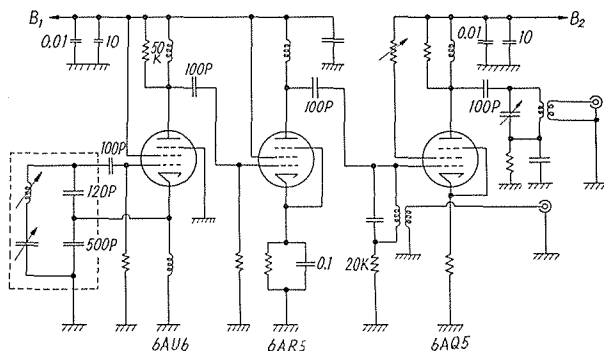


Fig. 3. Circuit diagrams of the 12.3 Mc/s oscillator and amplifier.

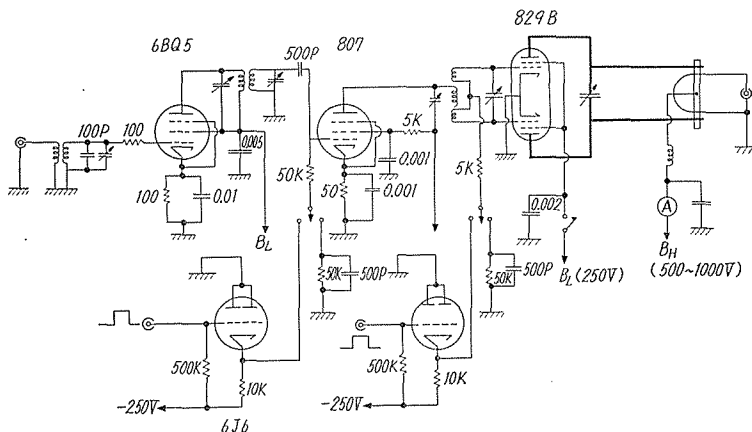


Fig. 4. Circuit diagram of the frequency multiplier with the gate tubes.

The steady-state proton NMR signal was observed by a Robinson type spectrometer.¹⁸⁾ Since T_1 of proton in this aqueous solution is relatively long and accordingly a weak rf power H_{1m} is desirable, this type is more convenient than the usual Pound-Knight type. The NMR signal was directly observed on an oscilloscope. The applied field was modulated at 60 c/s.

The pulsed NMR apparatus is as follows. The exciter consists of a pulsed oscillator and an rf amplifier. The receiver adopts 162 Kc/s straight amplification method instead of superheterodyne method and consists of a cascode signal amplifier and an rf signal amplifier. The circuit diagrams of them are shown in Fig. 6, 7 and 8. The constitution of the timing unit governing the

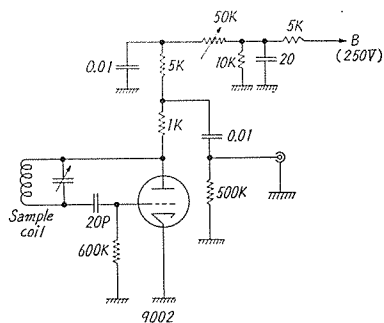


Fig. 5. Circuit diagram of the ESR spectrometer.

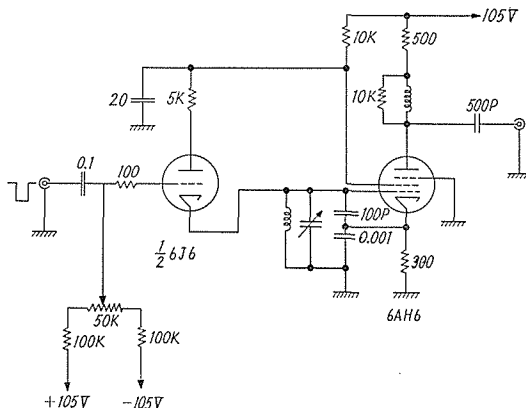


Fig. 6. Circuit diagram of the 162 Kc/s pulsed oscillator.

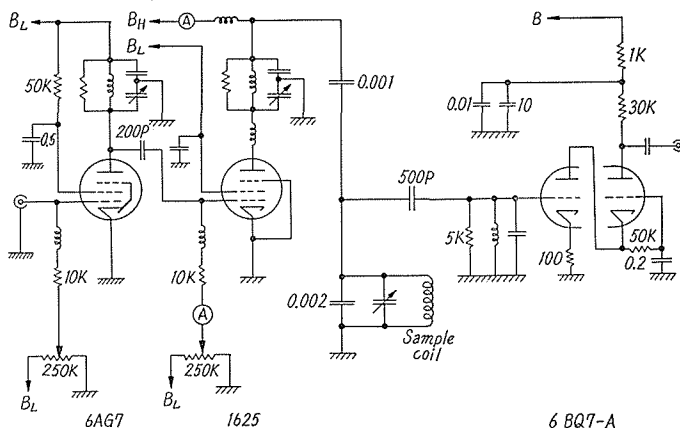


Fig. 7. Circuit diagrams of the 162 Kc/s rf amplifier and the cascode signal amplifier.

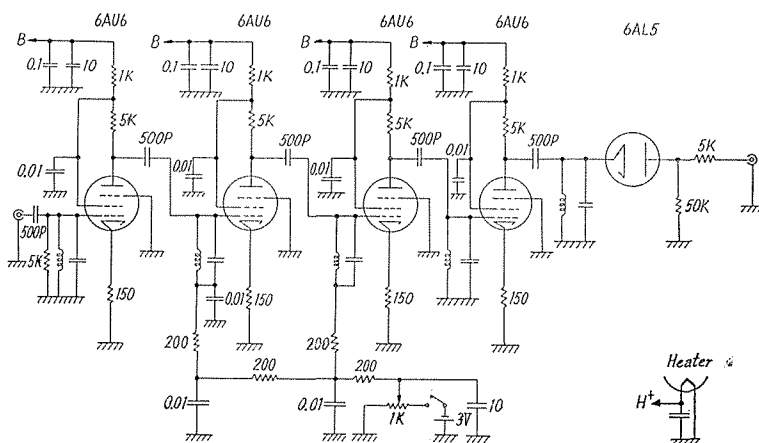


Fig. 8. Circuit diagram of the 162 Kc/s rf signal amplifier.

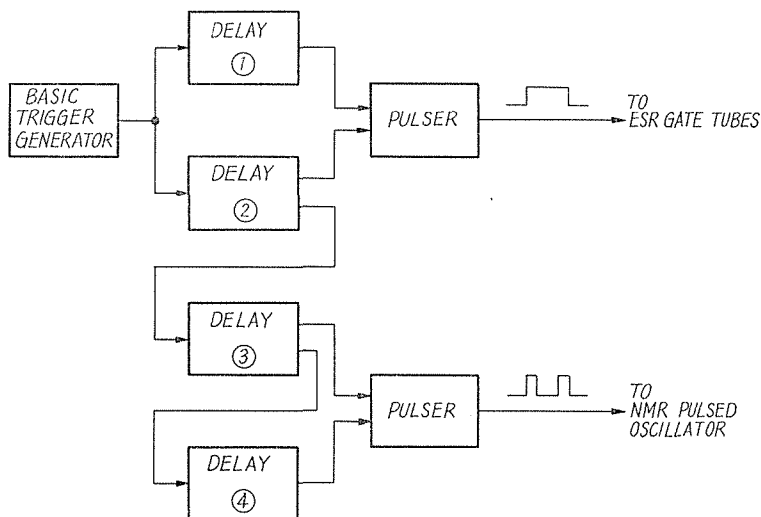


Fig. 9. Block diagram of the timing unit.

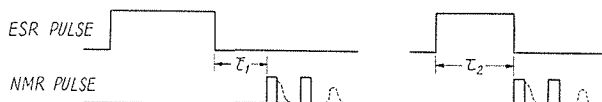


Fig. 10. Illustration of the pulsed double resonance method used in the low field measurements of T_1 and T_p . T_1 and T_p were measured by plotting the amplitude of the free induction or spin echo signal versus τ_1 and τ_2 , respectively.

pulsed double resonance experiment is shown in Fig. 9. The proton spin echo signal as well as the free induction decay was observed on a synchroscope. T_1 and T_p were measured by the combination of pulsed NMR and ESR methods as illustrated in Fig. 10.

The ESR and NMR coils are perpendicular to each other, the former being wound directly over the sample tube and the latter over the former. The sample volume is about 4 cm³.

(2) High field experiments

A transient double resonance experiment was performed at 3400 gauss, where the NMR frequency was 14.43 Mc/s and the ESR frequency was 9490 Mc/s. The apparatus is essentially the same as that used in another double resonance experiment made in our laboratory.¹⁹⁾ For the ESR spectrometer, a klystron V-58 C was used. The sample cavity was of rectangular TE₁₀₂ mode, including a 4 turn NMR coil inside. The maximum microwave power incident upon the cavity was about 180 mW. The sample was contained in a thin tube of 0.2 mm in diameter in order to avoid *Q*-dropping of the cavity. A Robinson type spectrometer was also used for NMR. The applied field was modulated at 380 c/s. The audio output of the spectrometer was observed on a triggered oscilloscope. The relaxation decay of polarization was observed upon switching off the microwave power, while the growth of polarization was observed upon switching it on. These transient signals were photographed, and T_1 and T_p were measured from the photographs.

The measurement of T_1 of proton at 2350 gauss (proton resonance frequency of 10 Mc/s) was made by use of a standard pulsed NMR method. T_1 was measured by applying a 90°-90° pulse sequence. The details of the apparatus is omitted in this article.

III. Results and Discussions

(1) Enhancement of NMR signal

At 38 gauss, when ESR of NO(SO₃)₂²⁻ ion was driven continuously, a proton signal with a large signal-to-noise ratio was observed directly on oscilloscope by both steady-state and pulsed method. Fig. 11 shows the steady-state and the free induction decay signal of proton in 0.01 M solution. The steady-state signal is thought to be considerably distorted because 60 c/s of field modulation is much higher than 1/ T_1 , T_1 being a fraction of a second. Accordingly reliable informations could not be obtained about the shape or width of the proton line. We could not detect the proton signal by either of two methods without driving ESR, therefore the enhancement factor was not determined. The use of a large amount of the sample was not advantageous, because the magnetic field inhomogeneity increased with it.

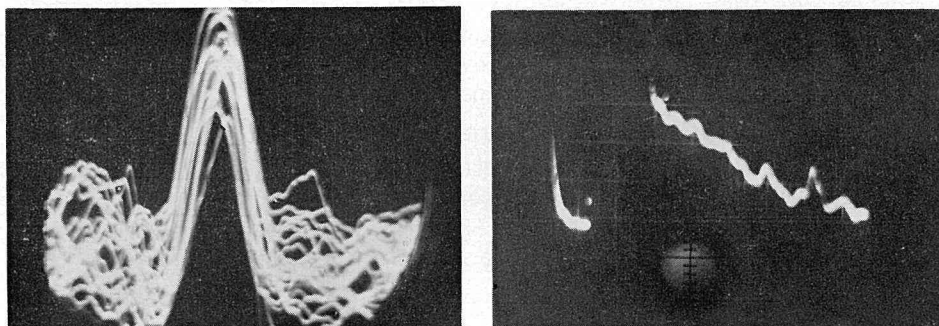


Fig. 11. Enhanced proton signals obtained by the steady-state (left) and the pulsed (right) NMR method on 0.01 M solution.

At 3400 gauss, a very small amount of the sample was used in order to avoid the Q-dropping of the microwave cavity. Again, the proton signal without ESR irradiation was not observed and the value of A could not be obtained either.

If the magnetization of electron spins of $\text{NO}(\text{SO}_3)_2^{2-}$ ion obeys the Bloch equations with relaxation times τ_1 and τ_2 , the ESR saturation factor s is written as follows:

$$s = \frac{S_0 - \langle S_z \rangle}{S_0} = \frac{\gamma_e^2 H_{1e}^2 \tau_1 \tau_2}{1 + \gamma_e^2 H_{1e}^2 \tau_1 \tau_2} \quad \dots\dots\dots(6)$$

Substitution of this into eq. (2) yields:

$$A = f \rho \frac{S_0}{I_0} \frac{\gamma_e^2 H_{1e}^2 \tau_1 \tau_2}{1 + \gamma_e^2 H_{1e}^2 \tau_1 \tau_2} \quad \dots\dots\dots(7)$$

Therefore, when plotting the inverse enhancement factor A^{-1} against the square of inverse ESR field strength H_{1e}^{-2} , a straight line should be obtained.³⁾ This was shown in Fig. 12 where the inverse NMR signal intensity proportional to A^{-1} was plotted, using the data obtained from the free induction decay signal at 38 gauss.

As mentioned briefly in Introduction, the enhancement observed by Allais is much smaller than the theoretically expected value of -110 in the case of "extreme narrowing".⁹⁾ This fact was attributed to the incomplete saturation of ESR. As we shall show in the next paragraph, however, the condition of "extreme narrowing" was not fulfilled in high field and accordingly the enhancement should reduce with increasing magnetic field. The estimation of the reduced enhancement factor can be made by calculating the coefficient ρ to be derived in the next paragraph using the value of correlation time obtained by T_1 measurements. The calculation yields $A \cong -30$ at 3300 gauss, in fair agreement with the value of -50 obtained by Allais. At least her result should not be attributed to the incomplete saturation by microwave power.

Recently, Müller-Warmuth and his coworkers made precise measurements of ρ on some organic free radical solutions over a wide range of magnetic field and found a similar decrease of the enhancement in high field.

(2) Proton spin-lattice relaxation time

T_1 of proton was measured at 38, 2350 and 3400 gauss for different concentrations of $\text{NO}(\text{SO}_3)_2^{2-}$ ion. The data are summarized in Fig. 13 where $1/T_1$ is plotted versus ion concentration. The data at 38 gauss were obtained by observing the spin echo signal. The linear dependence of $1/T_1$ upon ion concentration is clearly shown.

The remarkable feature is that T_1 at the higher fields is about two times longer than that at the low field in the measured range of the ion concentration. This shows that the correlation time τ_c associated with the random fluctuation of the

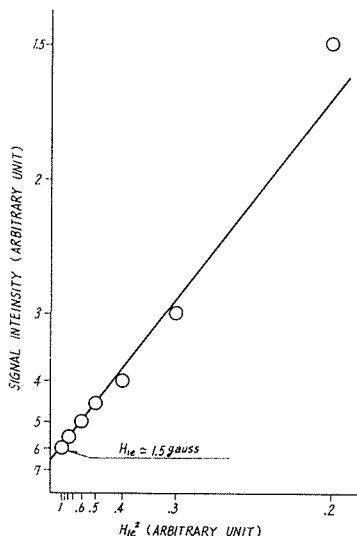


Fig. 12. Plot of the inverse of proton free decay signal intensity versus H_{1e}^{-2} . The data were obtained on 0.01 M solution.

proton-electron coupling is not very short and the "extreme narrowing" conditions ($\omega\tau_c \ll 1$) are not satisfied at the higher fields.

The contributions to proton T_1 can be divided into two parts, namely,

$$\frac{1}{T_1} = \frac{1}{T_{10}} + \frac{1}{T_1'} \quad \dots\dots\dots(8)$$

T_{10} represents the contribution from the coupling of protons between themselves, that is, T_1 of the pure water, while T_1' comes from the coupling with electrons. Actually, T_{10} includes the contribution from impurities such as dissolved oxygen or other paramagnetic ions. The extrapolated values of T_1 at both 38 and 3400 gauss to zero concentration coincide with T_1 of the pure water at 2350 gauss (2.8 sec), as shown in Fig. 13. This shows that T_{10} is almost field-independent.

The proton-electron coupling is assumed to be of dipolar type. The scalar coupling can be neglected because the enhancement of about -100 which is close to the theoretical value -110 was obtained at low field by Landesman.¹⁰⁾

The expression of T_1' of dipolar relaxation mechanism between two unlike spins I and S with Larmor frequencies ω_I and ω_S is as follows;²⁰⁾

$$\frac{1}{T_1'} = \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \left\{ \frac{1}{12} J_0(\omega_I - \omega_S) + \frac{1}{2} J_1(\omega_I) + \frac{3}{4} J_2(\omega_I + \omega_S) \right\}, \quad \dots\dots\dots(9)$$

where $J_i(\omega)$ is the spectral density of correlation function of the random fluctuation of the I - S coupling. If we consider that the random fluctuation is only due to the rotational motion, $J_i(\omega)$'s are expressed as follows:

$$\begin{aligned} J_0(\omega) &= \frac{24}{15 b^6} \frac{\tau_c}{1 + \omega^2 \tau_c^2}, \\ J_1(\omega) &= \frac{4}{15 b^6} \frac{\tau_c}{1 + \omega^2 \tau_c^2}, \\ J_2(\omega) &= \frac{16}{15 b^6} \frac{\tau_c}{1 + \omega^2 \tau_c^2}, \end{aligned} \quad \dots\dots\dots(10)$$

where b is the distance between proton and electron. The substitution of (10) and $S=1/2$ into (9) gives:

$$\frac{1}{T_1'} = \frac{\gamma_I^2 \gamma_S^2 \hbar^2 \tau_c}{10 b^6} \left[\frac{1}{1 + (\omega_I - \omega_S)^2 \tau_c^2} + \frac{3}{1 + \omega_I^2 \tau_c^2} + \frac{6}{1 + (\omega_I + \omega_S)^2 \tau_c^2} \right] \quad \dots\dots\dots(11)$$

In order to explain the observed field-dependence of T_1' , we assumed that the conditions of "extreme narrowing" ($\omega_S \tau_c, \omega_I \tau_c \ll 1$) are fulfilled at 38 gauss, but $\omega_S \tau_c$ can not be neglected against 1 at 2350 gauss. Then the expression (11) becomes:

$$\frac{1}{T_1'}_{low} = \frac{\gamma_I^2 \gamma_S^2 \hbar^2 \tau_c}{b^6} \quad \text{at 38 gauss,}$$

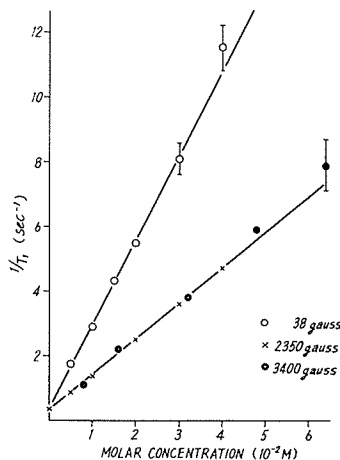


Fig. 13. Plot of $1/T_1$ versus ion concentration.

and

$$\frac{1}{T_1'_{high}} = \frac{\gamma_I^2 \gamma_S^2 \hbar^2 \tau_c}{10 b^6} \left(3 + \frac{7}{1 + \omega_S^2 \tau_c^2} \right) \text{ at 2350 gauss.}$$

The experimental values of T_1 on 0.01 M solution were 0.34 sec at 38 gauss and 0.70 sec at 2350 gauss. T_{10} was 2.8 sec at 2350 gauss but was not measured at 38 gauss though it is expected to have the same value from the above-mentioned field independence. By using these values and the ratio

$$\frac{T_1'_{low}}{T_1'_{high}} = \frac{1}{10} \left(3 + \frac{7}{1 + \omega_S^2 \tau_c^2} \right),$$

we obtain the value of $\tau_c = 5.6 \times 10^{-11}$ sec.

With the obtained value of τ_c we can also evaluate the coefficient ρ at high field, which will deviate from the low field value 1/2. The expression for ρ is as follows:²⁰⁾

$$\rho = \frac{-J_0(\omega_I - \omega_S) + 9J_2(\omega_I + \omega_S)}{J_0(\omega_I - \omega_S) + 18J_1(\omega_I) + 9J_2(\omega_I + \omega_S)}. \quad \dots\dots\dots(12)$$

We choose again the rotational model for representing the random fluctuation. Then substitution of (10) into (12) yields

$$\rho = \frac{-\frac{1}{1 + (\omega_I - \omega_S)^2 \tau_c^2} + \frac{6}{1 + (\omega_I + \omega_S)^2 \tau_c^2}}{\frac{1}{1 + (\omega_I - \omega_S)^2 \tau_c^2} + \frac{3}{1 + \omega_I^2 \tau_c^2} + \frac{6}{1 + (\omega_I + \omega_S)^2 \tau_c^2}}. \quad \dots\dots\dots(13)$$

The value of ρ at 3300 gauss was estimated to be 0.12 using the values $\tau_c = 5.6 \times 10^{-11}$ sec and $\omega_S = 2\pi \times 9.2$ kMc/s = 5.8×10^{10} sec⁻¹ and neglecting $\omega_I^2 \tau_c^2$ and $\omega_I \omega_S \tau_c^2$ as before.

The above expressions for T_1 and ρ based on the rotational model of random fluctuation can be generalized to include the translational motion, though calculations become very complicated. Müller-Warmuth et al. successfully applied the translational model to their results on some organic solutions obtained at various fields and temperatures.^{16,17)} Our results obtained so far can be fairly explained in terms of the simple rotational model.

(3) Proton polarization time

Fig. 14 shows oscilloscopic signals of the proton polarization growth and relaxation decay at 3400 gauss. It was found from the figure that these two processes had the same time constants ($T_p = T_1$), consistent with the prediction derived from the Solomon equation (1).

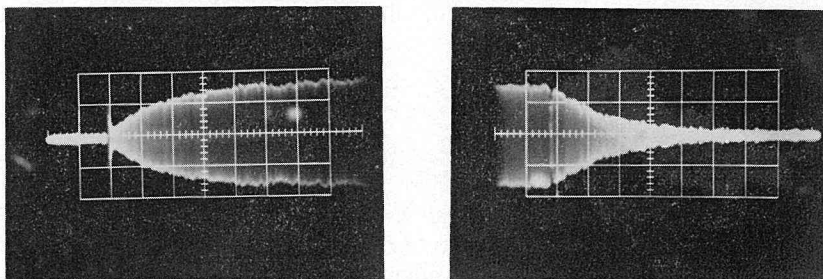


Fig. 14. Transient signals of proton observed at 3400 gauss: growth (left) and decay (right) of proton polarization.

At 38 gauss, an unexpected result was obtained: T_p is about two times longer than T_1 . Moreover, the polarization growth slightly deviates from an exponential form whereas the relaxation decay is quite exponential. The values of T_p at 38 gauss are shown in Fig. 15. T_p has a clear dependence upon ion concentration. Care was paid to eliminate the effect of rf heating during the ESR irradiation which may decompose the ion and consequently lengthen T_p . Furthermore, as is illustrated in Fig. 16, the growth curve is expressed as a difference of two exponential curves, one of which has the same time constant as the relaxation decay. The origin of the other time constant is quite unknown.

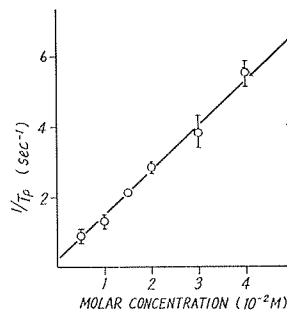


Fig. 15. Plot of T_p^{-1} versus ion concentration obtained at 38 gauss.

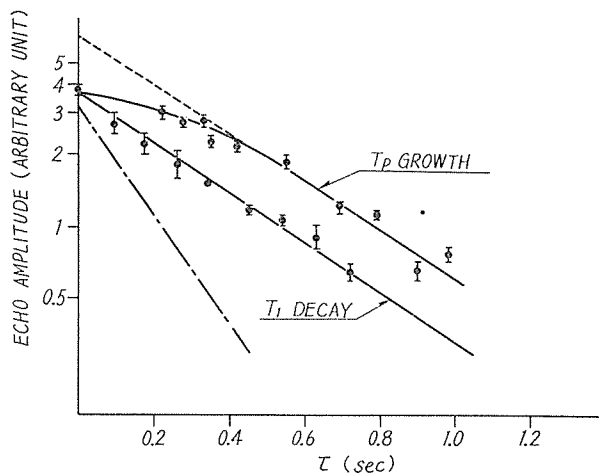


Fig. 16. Plot of the T_p growth together with the T_1 decay observed at 38 gauss. The growth curve is expressed as the difference between two exponentials (the upper dotted line and the lower broken line).

Only a qualitative explanation can be made, for the present, for the anomalous behavior described above. The proton-electron interaction is mainly responsible for the mechanism of proton relaxation and consequently that of dynamic polarization. If a very strong rf field stirs electron spins, the proton and electron spins may become highly decoupled. Therefore T_p may become longer than T_1 , for the ESR power is on during the polarization process while it is off during the relaxation process. The reason why T_p and T_1 are equal at 3400 gauss is that the microwave power is so weak that appreciable decoupling can not occur. Richards and White carried out a similar transient double resonance experiment on an organic free radical solution at 12500 gauss and concluded that T_p and T_1 were equal.¹⁷⁾ In their case, however, the microwave power was also very weak (about 200 mW), quite insufficient to break the proton-electron coupling. At present, no rigorous theory exists to explain our result.

IV. Concluding Remark

The sensitivity of NMR was largely increased by means of nuclear-electron double resonance, particularly in low field. This technique enabled us to obtain informations on the proton relaxation mechanism and on the effect of strong rf field upon the proton-electron interaction. Our measurements of the proton relaxation time clarified that at high field the "extreme narrowing" conditions were not satisfied in $\text{NO}(\text{SO}_3)_2^{2-}$ aqueous solution, and yielded the value of the correlation time associated with the random rotational motion. More studies at different fields such as several hundred gauss or over 10 kilogauss are necessary for the check of our simple model. The transient anomaly of the polarization growth was explained only qualitatively. The power-dependence study at other fields is desirable.

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