FACTORS INFLUENCING PROTON SPIN RELAXATION
IN PARAMAGNETIC ION SOLUTIONS

By

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1962

Submitted to the faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the degree of
MASTER OF SCIENCE
May, 1967

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ACKNOWLEDGMENT

The author wishes to express his gratitude to Dr. V. L. Pollak for his guidance throughout this study. Gratitude is also due the Army Research Office, Durham and the Research Foundation, Oklahoma State University for financial assistance for this project. A note of thanks is due to Richard Slater for devising the data reduction technique for the computer.

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INTRODUCTION

Nuclear magnetic reasonance is an experimental technique used to study liquids. When the liquid is placed in an external magnetic field a net magnetization occurs due to a net alignment with the field of the spins present in the solution. The decay of the components of this magnetization which are parallel and perpendicular to the external field are observed and the time constants of this decay are determined.

$\vec{M}$, the magnetization, is defined at any point within the sample as the average over a small region surrounding that point. The region is small enough so that the external field, $\vec{B}$, is uniform over it but large enough to include many spins.

The magnetization of such a volume element ∇V is given by:

$$\vec{M} = \frac{1}{\nabla V} \Sigma \vec{\mu}_i \tag{1}$$

where $\vec{\mu}_i$ is the magnetic moment of the individual nuclei present in the volume ∇V. The moments $\vec{\mu}_i$ point in random directions but with the application of a field there is a tendency for the moments to align with the field.

The equation of motion of $\vec{M}$ in an external field $\vec{B}$ is the same as that of a single element $\vec{\mu}_i$ or:

$$\frac{d\vec{M}}{dt} = \gamma \left[\vec{M} \times \vec{B} \right] \tag{2}$$

where γ is the gyromagnetic ratio of the nuclei in the solution.

$\vec{M}$ can be resolved into a parallel, $\vec{M}_z$, and a perpendicular component, $\vec{M}_{xy}$, to $\vec{B}.\vec{M}_{xy}$ will experience a torque and, therefore, will precess causing $\vec{M}$ to also precess. As thermal equilibrium is approached, $\vec{M}_{xy}$ must die out. This decay is given by:

$$\vec{M}_{xy}(t) = M_{xy}(o)\ e^{-t/T_2} \qquad (3)$$

The time constant of this decay is the transverse of spin-spin relaxation time, T_2.

When the spin system and the lattice are in thermal equilibrium the z component of the magnetization is given:

$$\vec{M}_o = \chi_o\vec{H} = \frac{\chi_o}{\mu_o}\vec{B} \qquad (4)$$

where χ_o is the magnetic susceptibility and μ_o is the permittivity of free space. The lattice is the material in which the magnetic moments, μ_i, are embedded.

If at any time $\vec{M}_z$ is not equal to $\vec{M}_o$, it will approach this value exponentially with a characteristic time T_1 called the thermal or longitudinal relaxation time. The rate of change of $\vec{M}_z$ due to thermal agitation alone is given by:

$$\frac{d\vec{M}_z}{dt} = \frac{\vec{M}_o - \vec{M}_z}{T_1} \qquad (5)$$

The solution to this equation is:

$$\vec{M}_z(t) = \vec{M}_o(1 - e^{-t/T_1}) \qquad (6)$$

The relaxation rates, $\frac{1}{T_{1,2}}$, are proportional to the square of the magnetic moments of neighboring spins. The magnetic moment of an electron is approximately 660 times as great as the magnetic moment of the protons. The magnetic moment of an paramagnetic ion results from its having unpaired electrons. The concentration of paramagnetic ions necessary to give a significant contribution to the relaxation rates is given by:

$$N_{ion} = \frac{\gamma^2_{prot}}{\gamma^2_{ion}} N_{prot} \approx 10^{-6} N_{prot} \tag{7}$$

Thus a very small concentration of paramagnetic ions will cause a large decrease in the relaxation times.

CHAPTER I

FLUIDS USED FOR TEMPERATURE CONTROL

General Requirements for a Tempering Fluid

The principal components of the NMR apparatus are the coils, the electronic equipment and the Haake Model NBS Constant Temperature Circulator. Since any ferromagnetic material may contribute to the nonuniformity of the earth's field, it has been necessary to place the coils a distance of 75 feet from the quonset building. This building houses the electronic equipment and the circulator.

The coils are connected to the quonset by two cables buried 1½ feet below the surface of the ground. The temperature of the sample in the coils must be controlled over a temperature range from -50°C to 100°C. A tempering fluid is used to accomplish this. The circulator regulates the temperature of this fluid and then circulates it through the buried pipes to the coil site and then back to the quonset.

Ideally, one tempering fluid should be used over the entire temperature range. However, a more realistic approach involves two liquids, one which can be used from 20°C to -40°C and one which can be used from 0°C to 100°C. This latter approach was the one first tried.

The liquid should be made basic with a pH of approximately 8.0. This will prevent corrosion of the circulator, pump, and the buried copper cable. The liquid also should not form a precipitate for this would cake the inside of the buried cable and reduce the flow of the liquid. It could cause possible harm to the circulator's pump.

The circulating liquid must have a relaxation time short enough so as not to add to or mask the signal from the sample. This means that the liquid must have a relaxation time, T_2, whose length is on the order of the transient arising from the electronic equipment or approximately 10 milliseconds. If it does not, then it must be altered in such a manner as to obtain the desired relaxation time.

The last restriction was easily resolved through the use of paramagnetic ions. The relaxation times of a solution of a paramagnetic salt varied inversely with the concentration of the ion present in the solution. The relaxation times can be shortened to the desired length just by increasing the concentration of the ion present in the liquid.

The following is a list of paramagnetic ions and the concentration necessary to produce a transverse relaxation time of 1 millisecond for an aqueous solution of the ion. The ions are listed in the order of their effectiveness in reducing T_2.[1]

1.) Manganese; 1.2×10^{19} ions/cc.; 1.99×10^{-2} M.
2.) Chromium; 2.75×10^{19} ions/cc.; 4.57×10^{-2} M.
3.) Iron (Fe^{+++}); 3.9×10^{19} ions/cc.; 6.48×10^{-2} M.
4.) Titanium; 4.9×10^{20} ions/cc.; 8.14×10^{-1} M.
5.) Copper; 5.25×10^{20} ions/cc.; 8.70×10^{-1} M.
6.) Nickel; 8.25×10^{20} ions/cc.; 1.37 M.
7.) Cobalt; 3.05×10^{21} ions/cc.; 5.07 M.

If paramagnetic salts of acids are to be used in the circulating fluid, then a base must be added. An additional problem then arises.

The hydroxies of paramagnetic ions are insoluble in water and other non-acidic solvents. It, therefore, was necessary to find a means of avoiding precipitation.

Aqueous Fluids Tried

The first fluid tried was an aqueous solution of $NiSO_4 \cdot 6H_2O$. This solution with a concentration of Ni^{++} of 5.5×10^{20} ions/cc. at 25°C was found to have a transverse relaxation time, T_2, of approximately 20 milliseconds. A concentration of 5.5×10^{20} ions/cc. has a signal which is not distinguishable from the transient. According to the table above, T_2 for this concentration should be on the order of 2 milliseconds.

The pH of this solution was measured by a Beckman Zeromatic pH Meter with a glass electrode. All measurements were made at room temperature.

Whenever a definite value of the pH is stated in the following discussion it was determined by this meter adjusted by a buffer solution in the proper pH range. When a range of values is given for the pH it was determined by a Alkacid Full Range pH Kit supplied by the Fisher Chemical Company.

The solution with a concentration of 5.5×10^{20} ions/cc. of Ni^{++} has a pH of 3.8. Three compounds were first tried to raise the pH; sodium bicarbonate, $NaHCO_3$; trisodium phosphate, $Na_3PO_4 \cdot 12\ H_2O$; and ammonium hydroxide, NH_4OH.

It was possible to only partially dissolve 0.19 gm. of $NaHCO_3$ in 50 ml. of the $NiSO_4 \cdot 6H_2O$ solution. The pH of the original solution was 3.8 and remained unaltered after the $NaHCO_3$ was added.

$NaHCO_3$ is readily soluble in water. It was possible to dissolve in 20 ml. of distilled water. The pH of this solution was 8.5. Then 0.01 ml. of the $NiSO_4 \cdot 6H_2O$ solution was added. A white precipitate was formed.

It was possible to partially dissolve 0.106 gm. of $Na_3PO_4 \cdot 12H_2O$ in 50 ml. of the $NiSO_4 \cdot 6H_2O$ solution. As in the case of $NaHCO_3$ the pH of the original solution was 3.8 and did not change after the addition of $Na_3PO_4 \cdot 12H_2O$.

However, 0.894 gm. of $Na_3PO_4 \cdot 12H_2O$ was readily soluble in water. The pH of this solution was 12.5. Then 0.01 ml. of the aqueous nickel solution was added. A greenish white precipitate was formed.

The precipitate formed in both cases included nickel hydroxide, $Ni(OH)_2$. Since $NiCO_3$ is insoluble in hot water and has a solubility of 0.0093 gm./100 ml. of water at 25 C, using $NaHCO_3$ as a base resulted in precipitate formation which was probably a combination of $Ni(OH)_2$ and $NiCO_3$. The amount of each would depend on the relative concentration of the ions involved.

Similarly $Ni_3(PO_4)_2 \cdot 8H_2O$ is insoluble in water. Therefore, both compounds, $Ni(OH)_2$ and $Ni_3(PO_4)_2 \cdot 8H_2O$ were present in the precipitate resulting from the use of $Na_3PO_4 \cdot 12H_2O$.

The third compound tried was ammonium hydroxide, NH_4OH. Since nickel forms water soluble amine complexes, it was hoped that enough NH_4^+ ion would be present to drive the reaction to the formation of the nickel amine complexes. The amount of NH_4OH that would be required proved to be prohibitive. In fact, 200 ml. of NH_4OH in a 500 ml. total solution was not enough to drive the reaction in the desired direction.

The precipitate was still present. In addition, the fumes due to the evaporation of NH_3 from this solution were intolerable at room temperature. At higher temperatures, an even larger amount of NH_3 would be given off.

The solution was next buffered with NH_4SO_4. This was accomplished by adding 75 ml. of the $NiSO_4 \cdot 6H_2O$ to 75 ml. of an NH_4SO_4 solution, both solutions having a concentration of 5.5×10^{20} ions/ml. The pH of the solution was 3.9. After 15 min. bluish white crystals in the shape of parallelopipeds were formed.

A similar result occurred when 50 ml. of the $NiSO_4 \cdot 6H_2O$ solution was added to 100 ml. of the NH_4SO_4 solution. The pH of this solution was 4.0. After 15 min. bluish white crystals were formed. They also had the shape of parallelopipeds. The only difference between these crystals and those formed previously was that these were somewhat smaller.

Next, 30 ml. of the $NiSO_4 \cdot 6H_2O$ solution was added to 120 ml. of the NH_4SO_4 solution. The pH of this solution was 4.2. After 15 min., whitish crystals were formed. They had a finer texture and were smaller than those formed in the above two cases.

The concentration of the components of these solutions were reduced in an effort to avoid crystallization.

The following solutions were prepared:

(A) 20 ml. of the $NiSO_4 \cdot 6H_2O$ solution, 20 ml. of the NH_4SO_4 solution and 155 ml. of water.

(B) 20 ml. of $NiSO_4 \cdot 6H_2O$ solution, 25 ml. of NH_4SO_4 solution and 150 ml. of H_2O.

(C) 20 ml. of $NiSO_4 \cdot 6H_2O$ solution, 15 ml. of NH_4SO_4

solution and 160 ml. of H_2O.

(D) 20 ml. of $NiSO_4 \cdot 6H_2O$ solution, 5 ml. of NH_4SO_4 solution and 170 ml. of H_2O.

A solution containing 29% ammonium hydroxide was added in varying amounts in an effort to raise the value of the pH. The results of these attempts are summarized below.

Solutions	A	B	C	D
Original pH	4.5-5.0	4.5-5.0	4.5-5.0	5.0
pH after addition of 0.2 ml. NH_4OH	7.0	7.0	7.0	7.2
pH after addition of 0.4 ml. NH_4OH	7.5	7.0-7.2	7.0-7.2	7.6
pH after addition of 0.8 ml. NH_4OH	8.0	7.6	8.0-8.5	8.0-8.5
pH of last solution after 1 day	7.2-7.6	7.0-7.2	7.2-7.6	7.2-7.6

The manganese ion does not form a water soluble amine complex but, nevertheless, it was tried. The salt $MnCl_2 \cdot 4H_2O$ was used. An aqueous solution of this salt with a concentration of 1.2×10^{19} ions/ml. of the Mn^{2+} ion was made up. This should have a T_2 of 0.9 to 2 milsec. It has a signal which is not distinguishable from the transient. However, the pH of such a solution is 5.3.

Upon addition of 0.1 ml. of NH_4OH a heavy white precipitate was formed. This was $Mn(OH)_2$. The air oxidized this precipitate to $MnO(OH)$. The color changed from white to brown.

Copper and iron were not tried due to their high electronegativity. Some of the metal parts on the circulator are composed of a nickel-steel alloy. Both ions were rejected since they would replace the nickel and plate out on the circulator.

An organic base, morpholine ($NHCH_2CH_2OCH_2CH_2$), was also tried. With both the nickel and the manganese, 0.01 ml. of morpholine produced a heavy white precipitate with the pH remaining at 3.8 and 5.3, respectively. The precipitate was probably the hydroxide of the respective ions.

We concluded that if an aqueous solution of a paramagnetic ion is to be used as the tempering fluid, then the solution must be acidic. The other alternative is to find some means to flush the precipitate out of the system after each run. Both an acidic and a basic solution were used to accomplish this. The system was then flushed out with distilled water. This procedure carried out with either solution took approximately half a day. Due to the length of time required, it does not seem practical. In addition, if NH_4OH is used, the pH of the circulating liquid must be constantly checked, since NH_3 will evaporate. Due to these reasons, the second alternative was rejected.

Non-Aqueous Fluids Tried

Two non-aqueous solvents were also investigated. These were ethylene glycol, C_2H_6O, and tetrachloroethylene, $Cl_2C=CCl_2$. These chemicals have the advantage that they could be used over a larger portion of the temperature range than the aqueous solutions.

Ethylene glycol has a T_2 of approximately 2.3 seconds. $MnCl_2 \cdot 4H_2O$ was used to reduce the relaxation time of this liquid. A solution of 60% $C_2H_6O_2$ and 40% water was used. This has a freezing point of -40°C.

A concentration of 1.2×10^{20} ions/ml. of the Mn^{2+} has no distinguishable signal. A concentration of 6×10^{19} ions/ml. of Mn^{2+}

has a signal which is barely detectable. The pH of this latter solution was between 6.0 and 6.4.

Several bases were used in an attempt to raise the pH of this solution without causing a precipitate. The following were placed in separate 50 ml. solutions of the ethylene glycol-$MnCl_2 \cdot 4H_2O$ solution; 0.005 gm. of $Na_3PO_4 \cdot 12H_2O$, 0.01 gm. of $NaHCO_3$, 0.04 gm. of NaOH, and 0.053 gm. of KOH. After five hours neither the $Na_3PO_4 \cdot 12H_2O$ nor the $NaHCO_3$ were completely dissolved. The pH of the solution remained between 6.0 and 6.4. In both cases a precipitate was formed. After 5 hours, the KOH and the NaOH were dissolved. The pH in both cases was 7.0. The color of the solution changed from clear to orange, being more intense with the NaOH than with the KOH. With both bases, a brown precipitate was formed.

When 0.05 ml. of NH_4OH was added to 50 ml. of the ethylene glycol solution the pH rose to a value between 7.6 and 8.0. However, a brown precipitate was formed.

Thus the ethylene glycol solution has the advantage of a higher pH than the aqueous Mn^{++} solution plus a wider temperature range.

The other fluid considered for possible use was tetrachloroethylene, $Cl_2C{=}CCl_2$. It is a colorless, clear, heavy liquid. It has a boiling point of 121.2°C at a pressure of 760 mm. of Hg. Its freezing point is −22.7°C. Its viscosity at 0°C is 0.44 cps., low enough to allow it to be circulated. It has the advantage of being nonflammable. It could be used over a considerable portion but not the entire temperature range.

Since its chemical composition does not involve any hydrogen atoms, it will not produce a signal. Therefore, it would not require the addition of any paramagnetic ions. Hence, the problem of precipitation would not be involved.

However, the chemical does present some problems. If water contaminates the liquid some hydrochloric acid will be formed and corrosion of the circulator can occur.

The fluid is toxic, but it is safer than most of the other chlorinated hydrocarbons. The probable safe concentration limit for a daily 8 hour exposure for this fluid is 100 parts per million. Methyl alcohol by comparison is rated at 200 parts per million.

Another disadvantage is that tetrachloroethylene is unstable. It can be oxidized in the presence of light and moisture yielding trichloroacetyl chloride, phosgene, trichloroacetic acid or various mixtures of these products. Of these three compounds phosgene is by far the most toxic having a safe concentration limit for a daily 8 hour exposure of 1 part per million. However, tetrachloroethylene can and is stabilized through the use of various inhibitors such as thymol.

Since the fluid, itself, is toxic, it should be used only if the circulating system, which is now essentially open, is converted into one which is closed. This could be accomplished by installing the proper ventilation system. It should include a hood which could be raised or lowered over the circulator.

The ventilation problem, however, was not the reason the fluid was discarded. One of the common industrial uses of tetrachloroethylene is degreasing metals. The possibility exists that the fumes from this chemical would degrease the motor on the circulator. This was the reason that the liquid was rejected.

However, the fluid is not very volatile and its vapor is five and one half times as heavy as air. Therefore, there is a possibility that, after more investigation, this liquid could be used.

The solution for the high temperature range which is now being used is the same as that which was used originally. This is an aqueous solution of $MnCl_2 \cdot 4H_2O$ with a concentration of the Mn^{2+} ion of 0.02M. As mentioned previously, the pH of this solution is 5.3 and has a T_2 of 1 milsec. at 40°C. The manganese ion was chosen since it is more effective than any of the other paramagnetic ions in shortening the relaxation time of water.

For the low temperature range, the two liquids considered were methyl alcohol, CH_3OH, and ethyl alcohol, C_2H_5OH. These fluids both have long inherent relaxation times and, therefore, paramagnetic ions must be added. Salts of nickel and manganese were again used to accomplish this.

A methanol solution of $NiSO_4 \cdot 6H_2O$ having a concentration of 5.5×10^{19} ions/ml. of the nickel ion was first tried. This is close to a saturated solution and the concentration of Ni^{++} ions cannot be greatly increased. This does not have a distinguishable signal. Theoretically, T_2 should be on the order of 6 milsec. The pH of this solution was 6.5.

When 0.01 ml. of an aqueous solution of KOH, NaOH, $Na_3(PO_4) \cdot 12H_2O$ or $NaHCO_3$ was added to the methanol-nickel solution a heavy white precipitate was formed. A similar precipitate was formed upon the addition of 0.01 ml. of a 29% NH_4OH solution, or 0.01 ml. of morpholine. The pH in all cases was unaffected.

A methanol solution of $MnCl_2 \cdot 2H_2O$ with a concentration of 1.2×10^{19} ions/ml. of the manganese ion was next tried. This solution does not have a distinguishable signal. Theoretically, T_2 for this solution should be on the order of 2 milsec. However, the concentration of Mn^{++} can be increased if necessary. The pH of this solution was between 6.4 and 6.8.

The same bases which were added to the nickel-methanol solution were also added to this solution. A brownish white precipitate was formed. The pH of the solution remained unchanged.

With the ethyl alcohol solution only the manganese ion was used. An ethanol solution with a concentration of 1.2×10^{20} ions/ml. of the Mn^{++} ion has no distinguishable signal while one with a concentration of 1.2×10^{19} ions/ml. has a T_2 of 4.1 milsec. A solution with a concentration of 6×10^{19} ions/ml. of Mn^{++} was finally used. Its signal does not differ significantly from the transient but its relaxation time, T_2, should be on the order of 1 milsec. The pH of this solution was between 6.4 and 6.8. Upon the addition of any of the bases used with the methanol-manganese solution a brownish white precipitate was formed. There seemed to be no significant difference in the precipitate formed with the methanol-manganese or the ethanol-manganese solutions. The pH, as with the methanol, remained unchanged.

Since methanol is approximately five times as toxic as ethanol, an ethanol-manganese solution was chosen as the tempering fluid used for low temperatures.

Conclusions

In conclusion, for high temperatures either the aqueous nickel or manganese ion solution may be used. The Mn^{++} solution is preferable since the manganese ion is more effective in reducing the relaxation time of water and its aqueous solution is less acidic than that of nickel.

For low temperatures, ethanol is preferable over methanol since it is less toxic. The Mn^{++} ion due to its higher solubility should be used as the added paramagnetic ion.

CHAPTER II

FIELD DEPENDENCE OF T_1 IN AQUEOUS Ni^{++} SOLUTION

General Theory

The addition of paramagnetic ions to water produces a marked reduction in the observed relaxation times for the protons of the water. This influence was first treated experimentally by Bloch, Hansen, and Packard.[2] It was first treated theoretically by Bloembergen, Purcell, and Pound.[3]

Proton relaxation in a solution of paramagnetic ions was first thought to arise solely from a dipole-dipole interaction between the ion and the water molecules in the coordination sphere. Using only this interaction, a theory was developed which predicted that the relaxation time T_1 should be independent of the frequency of the applied field. According to this theory, T_1 should be dependent only on the concentration and the viscosity at a given temperature. With this assumption, Bloembergen, Purcell and Pound[3] showed that T_1 and T_2 should be approximately equal. This approximate equality of T_1 and T_2 was also predicted by Solomon[4] in a later and more explicit formulation of the theory.

As more investigation was done, cases were discovered in which there occurred a marked deviation in the ratio between the transverse and the longitudinal times.[5,6] Furthermore, the ratio was found to be frequency dependent. The dipole mechanism provided no explanation for these abnormal ratios.

For T_1 to differ from T_2 by any significant degree there must be a randomly fluctuating perturbation with a long correlation time.[7] The correlation time, τ_c, for the dipole-dipole interaction was known to be of the same order of magnitude as the rotational correlation time of the coordination sphere of the paramagnetic ion or approximately 10^{-11} sec. An interaction which has the required long correlation time is the isotropic spin exchange interaction of the type $A\vec{I} \cdot \vec{S}$ between the electron spins $\vec{S}$ of the ion and the proton spins $\vec{I}$ in the coordination sphere.[8]

This exchange interaction, when considered along with the dipole-dipole interaction, was successful in explaining the experimental data. The total relaxation rates are the sum of the relaxation rates due to the dipolar interaction and the exchange interaction or

$$\frac{1}{T_1} = \frac{1}{T_1 dip} + \frac{1}{T_1 ex} \qquad (1)$$

$$\frac{1}{T_2} = \frac{1}{T_2 dip} + \frac{1}{T_2 ex} \qquad (2)$$

The expressions for the dipole interaction are given by

$$\left(\frac{1}{NT_1} \right)_{dip} = \frac{4}{30} \frac{s(s+1)\gamma_I^{\,2} g^2 \beta^2 p'}{r^6} \left[\frac{\tau_c}{1 + (\omega_I - \omega_s)^2 \tau_c^{\,2}} + \frac{3\,\tau_c}{1 + \omega_I^{\,2}\,\tau_c^{\,2}} + \right.$$
$$\left. + \frac{6\,\tau_c}{1 + (\omega_I - \omega_s)^2 \tau_c^{\,2}} \right] \qquad (3)$$

$$\left(\frac{1}{NT_2} \right)_{dip} = \frac{4}{60} \frac{s(s+1)\gamma_I^{\,2} g^2 \beta^2 p'}{r^6} \left[4\,\tau_c + \frac{\tau_c}{1 + (\omega_I - \omega_s)^2 \tau_c^{\,2}} + \frac{3\,\tau_c}{1 + \omega_I^{\,2} \tau_c^{\,2}} + \right.$$

$$+ \frac{6\,\tau_c}{1 + \omega_s^2\tau_c^2} + \frac{6\,\tau_c}{1 + (\omega_I+\omega_s)^2\tau_c^2} \qquad (4)$$

where ω_I and ω_s are the angular precessional frequencies of the nuclear spin $\vec{I}$ of the proton and the electron spin $\vec{s}$ of the ion, respectively. P' is the probability that a given proton will occupy a position in the coordination sphere of a paramagnetic ion in a 1M solution of the ion. N is the molar concentration of the paramagnetic ion. τ_c is the correlation time for the dipolar interaction. r is the ion-proton internuclear distance. γ is the proton gyromagnetic ratio and β is the Bohr magneton.

The appropriate expressions for the relaxation rates due to the exchange interaction are

$$\left(\frac{1}{NT_1}\right)_{ex} = \frac{2}{3}\, s(s+1) \left(\frac{A}{\hbar}\right)^2 P' \frac{\tau_e}{1 + (\omega_I-\omega_s)^2\tau_e^2} \qquad (5)$$

$$\left(\frac{1}{NT_2}\right)_{ex} = \frac{1}{3}\, s(s+1) \left(\frac{A}{\hbar}\right)^2 P' \left[\tau_e + \frac{\tau_e}{1 + (\omega_I-\omega_s)^2\tau_e^2}\right] \qquad (6)$$

where A is the exchange coupling constant, $\hbar$ is Planck's constant divided by 2π, τ_e is the correlation time for the exchange interaction, and all other symbols have the same meaning as in the expressions for the dipole interaction.

The expressions for the total relaxation rates are given by substituting the expressions for the dipole and the exchange interactions given by equations (3), (4), (5), and (6) into equations (1) and (2). When $\omega_I \ll \omega_s$ and $\omega_I \tau_c \gg 1$ the expressions for the total relaxation rates simplify to

$$\frac{1}{NT_1} = \frac{4}{30} \frac{s(s+1)\gamma_I^2 g^2 \beta^2 P'}{r^6} \left[3\tau_c + \frac{7\tau_c}{1 + \omega_s^2 \tau_c^2} \right] + \frac{2}{3} \frac{s(s+1)A^2 P'}{\hbar^2} \cdot \left[\frac{\tau_e}{1 + \omega_s^2 \tau_e^2} \right] \tag{7}$$

$$\frac{1}{NT_2} = \frac{4}{60} \frac{s(s+1)\gamma_I^2 g^2 \beta^2 P'}{r^6} \left[7\tau_c + \frac{13\tau_c}{1 + \omega_s^2 \tau_c^2} \right] + \frac{1}{3} \frac{S(s+1)A^2 P'}{\hbar^2} \cdot \left[\tau_e + \frac{\tau_e}{1 + \omega_s^2 \tau_e^2} \right] \tag{8}$$

These restrictions are not severe since τ_c is expected to be on the order of 10^{-11} sec. and $\omega_s = 650\ \omega_I$.

These equations show that the dipole contribution to T_1 and T_2 are approximately the same. Furthermore, at high frequencies where $\omega_s \tau_e \gg 1$, the exchange interaction eventually makes a negligible contribution to T_1 and equation (7) becomes

$$\frac{1}{NT_1} = \frac{4}{30} \frac{s(s+1)\gamma_I^2 g^2 \beta^2 P'}{r^6} \left[3\tau_c + \frac{7\tau_c}{1 + \omega_s^2 \tau_c^2} \right] \tag{9}$$

For this same frequency range, the equation for T_2 becomes

$$\frac{1}{NT_2} = \frac{4}{60}\,\frac{s(s+1)\gamma_I^{\,2}g^2\beta^2P'}{r^6}\left[\,7\tau_c + \frac{13\tau_c}{1+\omega_s^{\,2}\tau_c^{\,2}}\,\right] + \frac{1}{3}\,\frac{s(s+1)A^2P'}{r^6}\left[\tau_e\right] \tag{10}$$

At low frequencies when $\omega_s\tau_e \ll 1$ there is an exchange contribution to T_1. The relaxation rates, in this frequency range, are equal and are given by

$$\frac{1}{NT_1} = \frac{1}{NT_2} = \frac{4}{3}\,\frac{s(s+1)\gamma_I^{\,2}g^2\beta^2P'}{r^6}\,\tau_c + \frac{2}{3}\,\frac{s(s+1)A^2P'}{\hbar^2}\,\tau_e \tag{11}$$

At these frequencies, as evidenced by this equation, the relaxation rates are independent of frequency.

τ_c, the dipole correlation time, is related to the rotational time, τ_r, of the coordination sphere of the paramagnetic ion. However, τ_c may also depend upon the spin-lattice relaxation time of the electron spins, τ_s. This dependence of τ_c upon τ_r and τ_s is given by

$$\frac{1}{\tau_c} = \frac{1}{\tau_r} + \frac{1}{\tau_s} \tag{12}$$

The exchange correlation time, τ_e, is dependent upon the combined effect of the electron spin relaxation time, τ_s, and the mean lifetime of a proton in the coordination sphere, τ_h. The exchange correlation time, τ_e, is given by an expression similar to that for τ_c.

$$\frac{1}{\tau_e} = \frac{1}{\tau_h} + \frac{1}{\tau_s} \tag{13}$$

Proton relaxation is temperature dependent. The temperature effects can be explained by incorporating the proper temperature dependence of the several correlation times involved in the general relaxation expressions.

The lifetime of the protons in the coordination sphere, τ_h, is given by[9]

$$\tau_h = \tau_h{}^o e^{Vh/kT} \tag{14}$$

where V_h is the activation energy for the exchange of protons between the solvent and the coordination sphere. At room temperature, for the manganese ion, τ_h has a magnitude on the order of 10^{-8} sec.

The relaxation time of the electron spins, τ_s, is connected with the distortion of the coordination sphere due to collisions with water molecules outside this sphere. This distortion has a characteristic time denoted by τ_v. The electron spin relaxation time τ_s, for a quantum number 1 equal to two is given by[9]

$$\frac{1}{\tau_v} = \frac{12C_2{}^2\hbar^2}{55(s+1)} \left[\frac{\tau_v}{1 + \omega_s{}^2\tau_v{}^2} + \frac{4\,\tau_v}{1 + 4\,\omega_s{}^2\tau_v{}^2} \right] \tag{15}$$

where τ_v may be expressed as[9]

$$\tau_v = \tau_v{}^o e^{V_v/kT} \tag{16}$$

where V_v is the activation energy of the distortion of the coordination sphere of the ion.

Additional Frequency Dependence

Dohnanyi[10] has extended the theory using Kubo and Tomita's[11] method which is based on a perturbation expansion for the induced nuclear magnetization in terms of the interaction Hamiltonian of the spin system. This involves expanding the electron spin relaxation time into its longitudinal and transverse components. His effect predicts a small frequency dependence in addition to those mentioned above.

This dependence should occur in that frequency region where the exchange interaction is dominant or where $\omega_s\tau_e << 1$. It should be more pronounced for those ions where τ_s, the electron spin relaxation time, is dominant.

A decrease in temperature increases the length of τ_r, since this quantity varies directly with $e^{Vr/kT}$. Equation (15) shows that τ_s varies inversely with τ_V and directly with the quantity $(1 + \omega_s{}^2\tau_V{}^2)$. However, τ_V has an order of magnitude of 10^{-12} sec. and, over the fields employed, $\omega_s{}^2\tau_V{}^2$ is never greater than unity. Therefore, as the temperature is decreased τ_V is increased and τ_s is decreased. Thus, low temperatures increase the dominance of τ_s in determining τ_e.

Results

An attempt, using Ni^{++} with a constant temperature of 5°C, was made to verify Dohnanyi's theory. The longitudinal relaxation time, T_1 was investigated as a function of field. These results are shown in Figure 1. This graph indicates no additional frequency dependence other than that already predicted by equation (7).

$$\frac{1}{NT_1} = \frac{4}{30}\,\frac{s(s+1)\gamma_I{}^2 g^2 \beta^2 P'}{r^6}\left[3\tau_c + \frac{7\tau_c}{1 + \omega_s{}^2\tau_c{}^2}\right] + \frac{2}{3}\,\frac{s(s+1)A^2P'}{\hbar^2}\cdot \left[\frac{\tau_e}{1 + \omega_s{}^2\tau_c{}^2}\right] \qquad (7)$$

It does agree, however, with the curve predicted by this expression. Therefore, Dohnanyi's effect is either not present at all or it is too small to be detected by our apparatus.

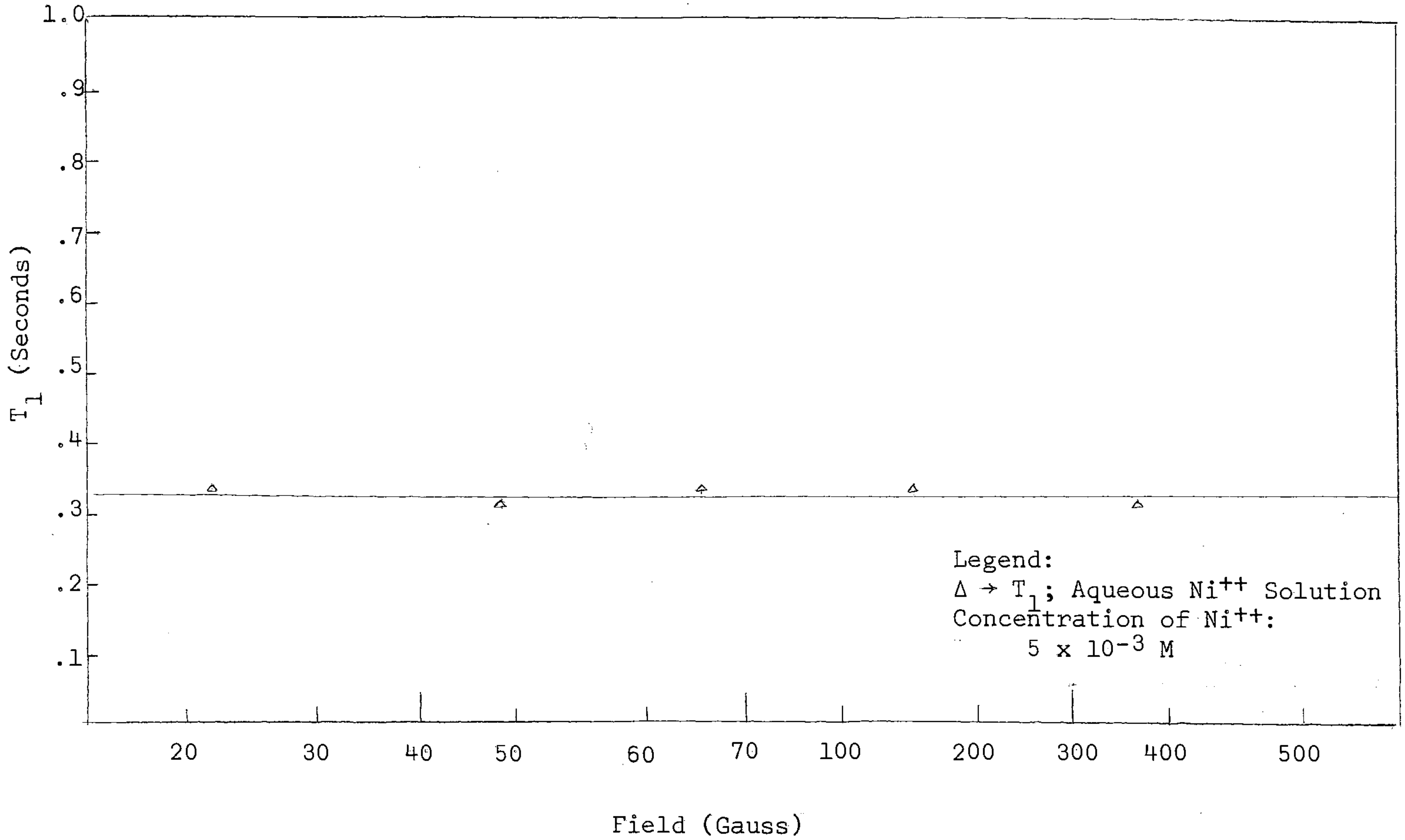

Figure 1. T_1 vs. Field for N_iSO_4 Solution at 5°C.

CHAPTER III

RELAXATION ENHANCEMENT OF AQUEOUS PARAMAGNETIC ION SOLUTIONS

General Theory

The effect of paramagnetic ions on the relaxation times of water can be used as a probe to investigate the chemical environment of the ion. The main contribution to the change in the proton relaxation times due to the presence of paramagnetic ions arises from an interaction between the ion and the water molecules in the coordination sphere of the ion. This effect depends not only on the concentration of the ion but also on the binding of the ion to other molecules which may be present in the solution.

When a water molecule is replaced by some other ligand in the coordination sphere of the ion the effectiveness of the ion in reducing the proton relaxation times should be expected to decrease. This effect has been observed when a chelating agent is added to an aqueous solution of the ion.[7] However, the relaxation times can under the proper circumstances decrease. That is, the effectiveness of the ion in reducing the relaxation times has been increased or enhanced. This occurrence is known as relaxation enhancement.[13]

When the ion is not chelated, that is, it is bound to a single, exterior site on a molecule, two degrees of rotational freedom are eliminated. The third may be reduced by the "friction" of the coordination sphere against the molecule. When chelation occurs rotation is stopped completely.[12] Therefore, whether chelation is present or not, the rotational correlation time is increased, $\frac{\tau_r^*}{\tau_r} > 1$, where the asterisk denotes values for the bound ions.

If τ_s and τ_h do not change appreciably and τ_r is the dominant correlation time, then $\frac{\tau_c^*}{\tau_c} > 1$. Since the relaxation time, NT_1, is inversely proportional to τ_c, an increase in τ_c would cause a corresponding decrease in the longitudinal relaxation time if this were the only factor involved.

However, NT_1, is also inversely proportional to the probability, P', that a proton is in the coordination sphere of the ion which in turn is proportional to the number of protons in the sphere. When chelation occurs, the chelating agent occupies two or more sites in the sphere. If chelation does not occur but the added molecule competes successfully with the water molecules for a coordination site then one or more of the non-aqueous ligands will occupy sites in the coordination sphere. In any case, the ratio of P'^* to P' will be less than one. This decrease in P' will cause an increase in NT_1. Therefore, for the relaxation time to decrease, the increase in the dipole correlation time must be sufficient to overshadow the decrease in the value of P'.

An enhancement factor can be defined as[13,16]

$$\epsilon = \frac{\frac{1}{T_1^*} - \frac{1}{T_1^*(0)}}{\frac{1}{T_1} - \frac{1}{T_1(0)}} \approx \frac{T_1}{T_1^*} \approx \frac{P'^*\tau_c^*}{P'\tau_c} \qquad (1)$$

where $\frac{1}{T_1^*(0)}$ and $\frac{1}{T_1(0)}$ are the longitudinal proton relaxation rates in the solution under study and in water with no paramagnetic ions added.

The last approximation in this equation is valid only when there is negligible exchange contribution to the relaxation time when $\omega_s \tau_c^* \ll 1$ and $\omega_s \tau_c \gg 2$. These conditions do not prevail over the entire frequency range which can be investigated by our apparatus. However, if this approximation is deleted, equation (1) becomes

$$\epsilon = \frac{\frac{1}{T_1^*} - \frac{1}{T_1^*(0)}}{\frac{1}{T_1} - \frac{1}{T_1}} \approx \frac{T_1}{T_1^*}$$

which is valid over our entire frequency range.

The observed enhancement of proton relaxation is a weighted average of that due to the free ions and that due to the bound ions. Thus, another form for the enhancement factor other than that given above is the following:

$$\epsilon = \frac{M_f}{M_t} \epsilon_f + \frac{M_b}{M_t} \epsilon_b \tag{2}$$

where M_t is the total ion concentration; ϵ_f, the enhancement of the free ions, is equal to 1 by definition; and ϵ_b is the enhancement of the bound ions.

The magnitude of ϵ can be in any one of three numerical ranges. These are summarized below:

I. $\epsilon = 1$. The ion is in solution but is not bound. This value of ϵ can also occur when the ion is bound to an exterior site on the molecule but τ_r is not the dominant correlation time.

II. $\epsilon > 1$. The ion is bound to an exterior site.

III. $\epsilon < 1$. The accessibility of the ion to the solvent water protons has been reduced. In this case $P^* < P$. It could also occur when the ion is bound to an accessible site but the rotational correlation time, τ_r, is not dominant, i.e., the binding reduces τ_s to the point that $\tau_s < \tau_r$.

Using the fact that the total concentration of the ion is equal to the sum of the concentrations of the free and the bound ions, equation (2) can be solved for the concentration of either the free or the bound ion in terms of the total ion concentration and the enhancement parameter to yield:

$$M_f = \left(\frac{\varepsilon_b - \varepsilon}{\varepsilon_b - 1} \right) M_t \tag{3}$$

$$M_b = \left(\frac{\varepsilon - 1}{\varepsilon_b - 1} \right) M_t \tag{4}$$

The association constant for the ion to the added molecule is defined by:[13]

$$K_a = \frac{[M_b]}{[M_f][P_f]} \tag{5}$$

where $[P_f]$ represents the concentration of the unfilled binding sites in the solution. P_f is given by:

$$P_f = nP_t - M_b \tag{6}$$

where n is the number of binding sites per molecule of added ligand with the association constant K_a, and P_t is the total concentration of the added ligand. Combining equations (3), (4), (5), and (6) yields:

$$K_a = \frac{(\epsilon - 1)(\epsilon_b - 1)}{(\epsilon_b - \epsilon)[nP_t(\epsilon_b - 1) + M_t(1 - \epsilon)]} \tag{7}$$

To determine the constants K_a, M_f, and M_b from equations (3), (4), and (7) the enhancement of the bound ion, ϵ_b, and the number of binding sites, n, must be known. The value of ϵ_b is obtained by extrapolating a plot of ϵ versus the added ligand concentration to infinite ligand concentration.[13] From the double reciprocal plot of Hughes and Klotz[14] n and K_a are obtained. For this plot the concentrations of the free and bound ion are determined from equations (3) and (4).

A physically more significant factor is the relaxation rate per paramagnetic ion defined by:

$$\frac{R}{N} = \frac{\frac{1}{T_1^*} - \frac{1}{T_1^*(0)}}{N} \tag{8}$$

where N is the ion concentration and $T_1(0)$ is the relaxation rate of the solution without the presence of the ion. This equation yields a measure of the effectiveness of a paramagnetic ion originally in the solution as a proton relaxing agent.

Another method of presenting the experimental results is through the use of the effective proton relaxation rate, R_1(eff.). This rate is determined by contributions from R_1^* due to the number of bound ions and R_1 arising from the free ions. R_1(eff.) is given by:[7]

$$\frac{R_1(\text{eff})}{N} = \frac{R_1^*}{N_o} + \frac{R_1}{(N - N_o)} \tag{9}$$

where N_o is the capacity of the added molecule for the ion. This equation is valid only when $N > N_o$ with the assumption that N_o ions are bound. When $N < N_o$, it is assumed that all the ions are bound to a molecule. In this case, the last term in equation (9) is deleted and $R_1(\mathrm{eff})/N$ is equal to R_1/N.

$R_1(\mathrm{eff})$ may be determined only if the added ligand is a large, non-chelating molecule. This is due to the assumption involved in equation (9). That is that no more than one of the added molecules is present in the coordination sphere of the ion.

Results

Several chemicals were added to a 3×10^{-4} M. solution of $CuCl_2 \cdot 2H_2O$. They were p-aminobenzoic acid, $H_2NC_6H_4CHCOONH$; methionine, $CH_3SCH_2CH_2COONH_3$; tyrosine, $OHC_6H_4CH_2CHCOONH_3$; and pyridine, C_5NH_5. The results of these attempts are listed in Tables I, II, III, IV, and V.

The concentration of these chemicals was varied holding the copper ion concentration constant. The temperature was held constant at 40°C and the solutions were studied as a function of field.

As evidenced by the listed values of ϵ, enhancement was not exhibited to any significant degree by the first three chemicals named. The proximity of ϵ to a value of one indicates that there exists little if any interaction between these chemicals and the copper ion.

These are three of the many amino acids. It was hoped that the work done on these chemicals would lead to an investigation of the coalescence of a number of amino acids which would contain one or more of the above chemicals. By studying each acid separately and comparing these results with those obtained from the acid formed through coalescing a number of acids, knowledge concerning the position of the binding sites of the ion could be obtained. Such information could be of biological and biophysical value.

Pyridine is an organic base and when added to the copper solution copper hydroxide appeared as a precipitate. This was avoided by making the solution acidic. Two acids, 2×10^{-2} M. of HCL and 2×10^{-2} M. of perchloric acid, were used to achieve this. Perchloric acid is preferable over hydrochloric acid since the perchlorate ion does not coordinate and, therefore, would not interfere with the enhancement.

With both types of solutions of pyridine the values of the enhancement factor were very close to unity. This would indicate a very small interaction between the ion and the pyridine. This could be due to the fact that the solutions were too acidic.

Nevertheless, two of the solutions using HCL as an acidifying agent showed some indication of enhancement. The concentration of pyridine in these solutions was 1×10^{-3} M. and 3×10^{-4} M. The values of the enhancement factor for the solutions containing perchloric acid were slightly smaller. However, there was some indication of enhancement. Reducing the acidity of the solutions could possibly increase the enhancement. This can be determined only by further study of the enhancement as a function of pH.

In addition to the chemicals mentioned above, sodium carboxymethylcellulose, CMC-7AT, was used as an enhancement agent.

Since sodium carboxymethylcellulose is a long chained polymer, the molarity of CMC-7AT involves the number of structural units present; a structural unit of CMC-7AT is a substituted anhydroglucose unit ($C_6H_{10}O_5$) of the parent carboxymethylcellulose compared with .7 sodium carboxylmethyl groups (CH_2COONa) replacing .7 hydrogens in an anhydroglucose unit. Therefore, a structural unit of sodium carboxylmethylcellulose has a chemical formula of $C_6H_{9.3}O_5\ (CH_2COONa)_{.7}$ with a molecular weight of 281.53 gm. Thus, one mole of CMC-7AT would weigh 2.8.153 gm. and contain approximately 6.0×10^{23} structural units.

It was possible to add only 6×10^{-4} M. of CMC-7AT to the 3×10^{-3} M. $CuCl_2$ solution without forming a precipitate. However, no precipitate was formed when sodium carboxymethylcellulose was added to an aqueous solution of 1×10^{-4} M. of $MnCl_2 \cdot 4H_2O$.

Unlike the chemicals mentioned above, CMC-7AT effected a noticeable degree of enhancement. The greatest enhancement was exhibited by the solution containing 1×10^{-3} M. of sodium carboxymethylcellulose. As the concentration of CMC-7AT is decreased the number of binding sites for the manganese ion decreases and the relaxation time, T_1, approaches that of an aqueous solution of Mn^{++}.

The increase in T_1 in Figures 4 and 5 as the concentration of CMC-7AT increases beyond 1×10^{-3} M. could arise from the fact that the number of complexes with more than one coordination site filled by sodium carboxymethylcellulose increases. This would result in a decrease in the accessibility of Mn^{++} ions to the protons of the bulk solution. It would also cause the number of protons in the coordination sphere of the ion to decrease from six to four or less. As the concentration of CMC-7AT is increased, the relaxation time would approach T_1 of water.

From the data available it was possible to obtain some idea of the magnitude of the total enhancement, ϵ; the enhancement of the bound ions, ϵ_b; the concentration of the free and bound manganese ions, M_f and M_b; and also the dissociation constant of the manganese ion from CMC-7AT, K_D. The dissociation constant is the reciprocal of the association constant and is given by:

$$K_D = \frac{M_f P_f}{M_b} = \frac{(M_t - M_b)P_f}{M_b} \qquad (10)$$

M_b is given in terms of the enhancement in equation (4):

$$M_b = \left(\frac{\epsilon - 1}{\epsilon_b - 1} \right) M_t \qquad (4)$$

Substituting this expression for M_b in equation (10) and solving for $\frac{1}{\epsilon}$ yields:

$$\frac{1}{\epsilon} = \frac{1}{\epsilon_b} \left[\frac{K_D}{P_f + \left(\frac{K_D}{\epsilon_b} \right)} + \frac{P_f}{P_f + \frac{K_D}{\epsilon_b}} \right] \qquad (12)$$

As the total sodium carboxymethylcellulose becomes large compared to K_D/ϵ_b, P_f approaches P_t and the quantity, $P_f + K_D/\epsilon_b$ may be approximated by P_t. This yields:

$$\frac{1}{\epsilon} = \frac{K_D}{\epsilon_b} \left(\frac{1}{P_t} \right) + \frac{1}{\epsilon_b} \qquad (13)$$

Thus, at high CMC-7AT concentrations, a plot of the reciprocal of the observed enhancement against the reciprocal of the total CMC-7AT concentration should yield a straight line whose slope is equal to K_D/ϵ_b. The intercept along the $\frac{1}{\epsilon}$ axis should yield $\frac{1}{\epsilon_b}$. The value of ϵ_b obtained from such an analysis was 1.457.

The deviation of the curve in Figure (2) from straight line plots is caused by an asymptotic approach to a unit value for $\frac{1}{\epsilon}$ as the concentration of CMC-7AT is decreased. This is the value of $\frac{1}{\epsilon}$ for an aqueous solution of the manganese ion.

The association constant, K_a, can also be found from this plot. It is easiest to find at a value of the enhancement equal to one half of $\epsilon_b + 1$. At this value by equation (4),

$$M_b = \left(\frac{\epsilon - 1}{\epsilon_b - 1} \right) M_t \tag{4}$$

the concentration of the bound manganese ion is equal to one half of the total concentration of the ion. The association constant, K_a, was given in equation (7) as

$$K_a = \frac{(\epsilon - 1)(\epsilon_b - 1)}{(\epsilon_b - \epsilon)[nP_t(\epsilon_b - 1) + n_t(1 - \epsilon)]} \tag{7}$$

For a value of ϵ of one half of $\epsilon_b + 1$, K_a is given by

$$K_a = \frac{1}{[nP_t - \frac{M_t}{2}]} \tag{14}$$

As mentioned above, $M_t/2$ at this value of ϵ, is equal to M_f. Therefore, equation (14) is equivalent to

$$K_a = \frac{1}{[nP_t - M_f]} \tag{15}$$

By equation (6)

$$P_f = nP_t - M_f \tag{6}$$

the expression for the association constant becomes $K_a = \frac{1}{P_f}$.

Using the above value of 1.45 for ϵ_b, the enhancement ϵ is 1.22 when it is equal to one half of $\epsilon_b + 1$. From Figure (2) for this value of ϵ, the total concentration of CMC-7AT is 1.63×10^{-4} M. The total manganese ion concentration for this plot was held constant at 1×10^{-4} M. Therefore, the bound manganese ion concentration, which is one half the total manganese concentration at this value of ϵ, is 5×10^{-5} M. By equation (6), assuming 0.7 binding sites per structural unit of CMC, the concentration of free sodium carboxymethylcellulose is 6.41×10^{-5} M. Taking the reciprocal yields a value of 1.60×10^4 M^{-1} for the association constant, K_a.

K_a was also calculated using equation (7) and assuming a value of 1.45 for ϵ_b. The results of these calculations are listed in Table VI. These calculations gave an average value for K_a of 1.03×10^4 M^{-1}.

The value of ϵ_b is only as accurate as Figure (2). For this value to be anything more than a rough estimate, the number of points in this plot should be increased by at least a factor of two.

Due to this lack of accuracy in determining ϵ_b, the values of K_a, M_f, and M_b are in doubt. No information concerning the strength of the binding sites could be obtained. Also, the validity of the assumption that there are 0.7 binding sites per molecule of CMC-7AT could not be verified.

This assumption could be checked only if the Mn^{++} concentration was varied holding the sodium carboxymethylcellulose concentration constant. The relaxation time T_1 would then be plotted against the concentration of the manganese ion. When the concentration of Mn^{++} exceeded the capacity of CMC-7AT for the ion the T_1 curve would approach the T_1 curve for an aqueous solution of the manganese ion.

A correction of the observed T_1 and T_2 was made with the values of the intrinsic T_1 and T_2 of H_2O using:

$$\frac{1}{T} = \frac{1}{T^{obs}} - \frac{1}{T^{H_2O}} \qquad (10)$$

T is the relaxation time due to the solution alone. T^{obs} is the observed relaxation time and it appears in the Tables at the end of this chapter under the heading Raw Data. T^{H_2O} is the intrinsic relaxation time of H_2O. The value of 3.66 sec. given by Koegeboehn[17] was used for $T_1^{H_2O}$. A more complete discussion of this correction has been given by Mitchell.[18]

R was also calculated. The relaxation times of sodium carboxymethylcellulose are the same as those for water. Therefore, the curves of R plotted against both the field and the concentration of CMC-7AT are the same as the T_1 curves.

The enhancement factor decreases with the field. A possible explanation arises from equation (11) of Chapter 2.

$$\frac{1}{NT_1} = \frac{4}{3}\,\frac{s(s+1)\gamma_I^2 g^2 \beta^2 P'}{r^6}\,\tau_c + \frac{2}{3}\,\frac{s(s+1)A^2 P'}{\hbar^2}\,\tau_e$$

This equation shows that T_1 is inversely proportional to τ_c. Similarly, after the chelating agent has been added, T_1^* is inversely proportional to τ_c^*.

The dipole correlation time, τ_c, is given by equation (11) of Chapter 2:

$$\frac{1}{\tau_c} = \frac{1}{\tau_r} + \frac{1}{\tau_s} \qquad (11)$$

The rotational correlation time, τ_r, is given by[8]

$$\tau_r = \tau_r^{o}\, e^{-Vr/kT} \tag{12}$$

τ_r thus depends only on the temperature. The electron spin relaxation time is given by equation (12) of Chapter 2:

$$\frac{1}{\tau_s} = \frac{12C_2^{2}\hbar^{2}}{5s(s+1)} \left[\frac{\tau_V}{1 + \omega_s^{2}\tau_V^{2}} + \frac{4\,\tau_V}{1 + 4\omega_s^{2}\tau_V^{2}} \right] \tag{12}$$

Thus, except for the frequency range where $\omega_s\tau_V \ll 1$, a decrease in field will cause τ_s to also decrease.

If τ_r is the dominant correlation time, then τ_c would depend only on the temperature. The dependence of τ_c on the temperature can be reduced, if not completely eliminated, by the addition of a chelating agent. This could cause the rotational correlational time, τ_r^{*}, to increase in length to such an extent that τ_s^{*} becomes the dominant correlation time. If this were the situation, then τ_c would depend primarily upon the temperature while τ_c^{*} would be directly proportional to the field. T_1, then, would depend upon the temperature while T_1^{*} would be inversely proportional to the field:

$$T_1 \propto \frac{1}{\tau_c} \propto \frac{1}{\tau_r} \propto e^{Vr/kT}$$

$$T_1^{*} \propto \frac{1}{\tau_c^{*}} \propto \frac{1}{\tau_s^{*}} \propto \frac{1}{s^{2}}$$

The enhancement factor is given by equation

$$\varepsilon \approx \frac{T_1}{T_1^{*}}$$

Therefore,

$$\epsilon \approx \frac{T_1}{T_1^{*}} \propto \frac{\tau_c^{*}}{\tau_c} \propto \frac{{}_{s}^{2}}{e^{Vr/kT}}$$

Therefore, a decrease in field would cause a corresponding decrease in the enhancement factor.

The graphs in Figure (3) show the usual dependence of the relaxation time, T_1, upon the field. The field is increased from the region where the quantity $\omega_s\tau_e$ is much less than unity to the region where $\omega_s\tau_e$ is approximately unity. In the first region there is a negligible contribution from the exchange term to the relaxation time, T_1. In the second region there is a significant contribution from the exchange term.

The graphs of Figures (4) and (5) of T_1 versus the concentration of CMC-7AT show a minimum. As the concentration of CMC-7AT is increased beyond this minimum point, the graph approachs the value of T_1 for water. As mentioned previously, this could be due to more than one coordination site of the manganese ion being filled by CMC-7AT. As the concentration of CMC-7AT is decreased the curves approach the value of T_1 of the manganese solution.

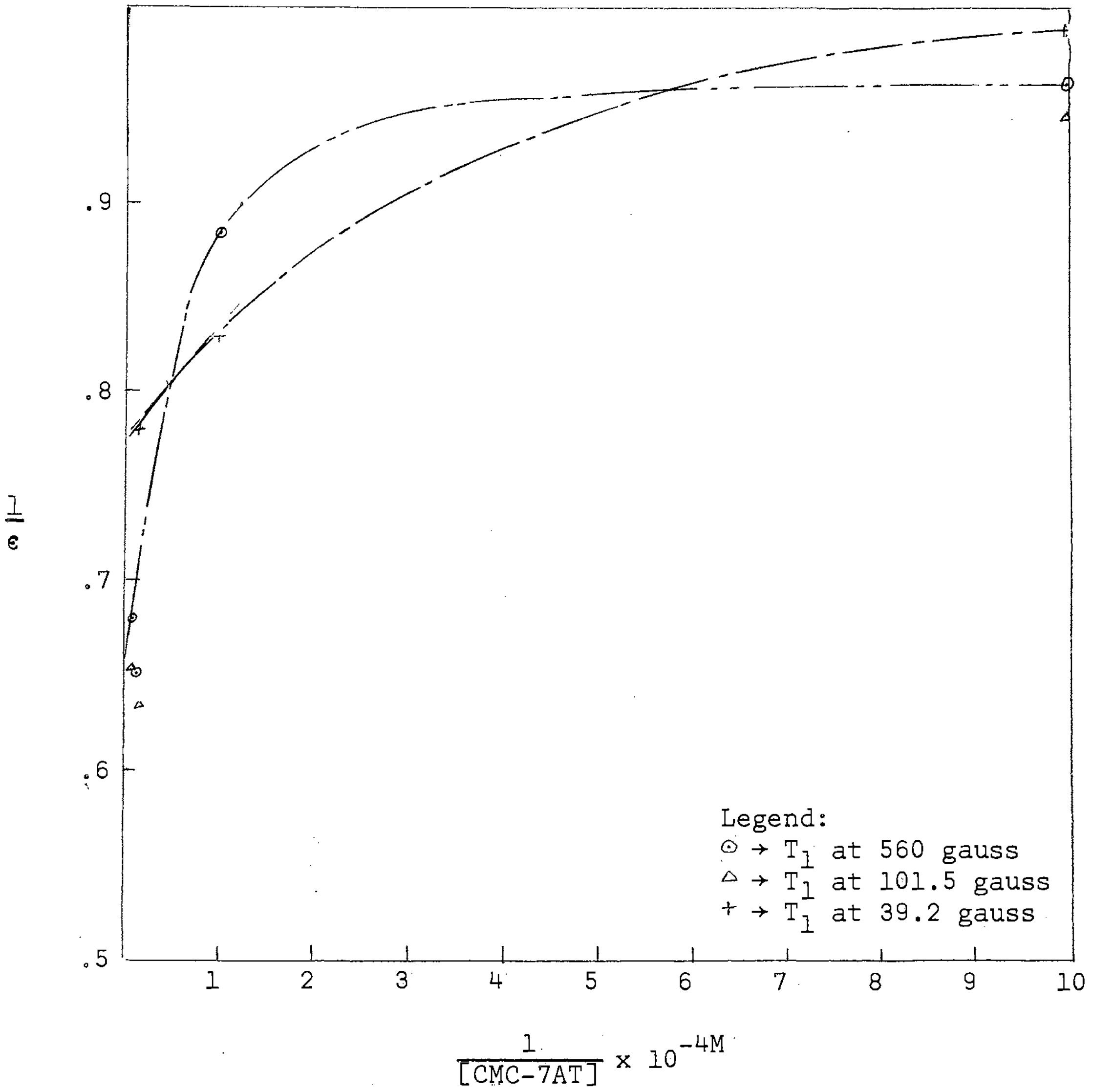

Figure 2. $\frac{1}{\varepsilon}$ vs. Concentration of CMC-7AT

at 25° C.

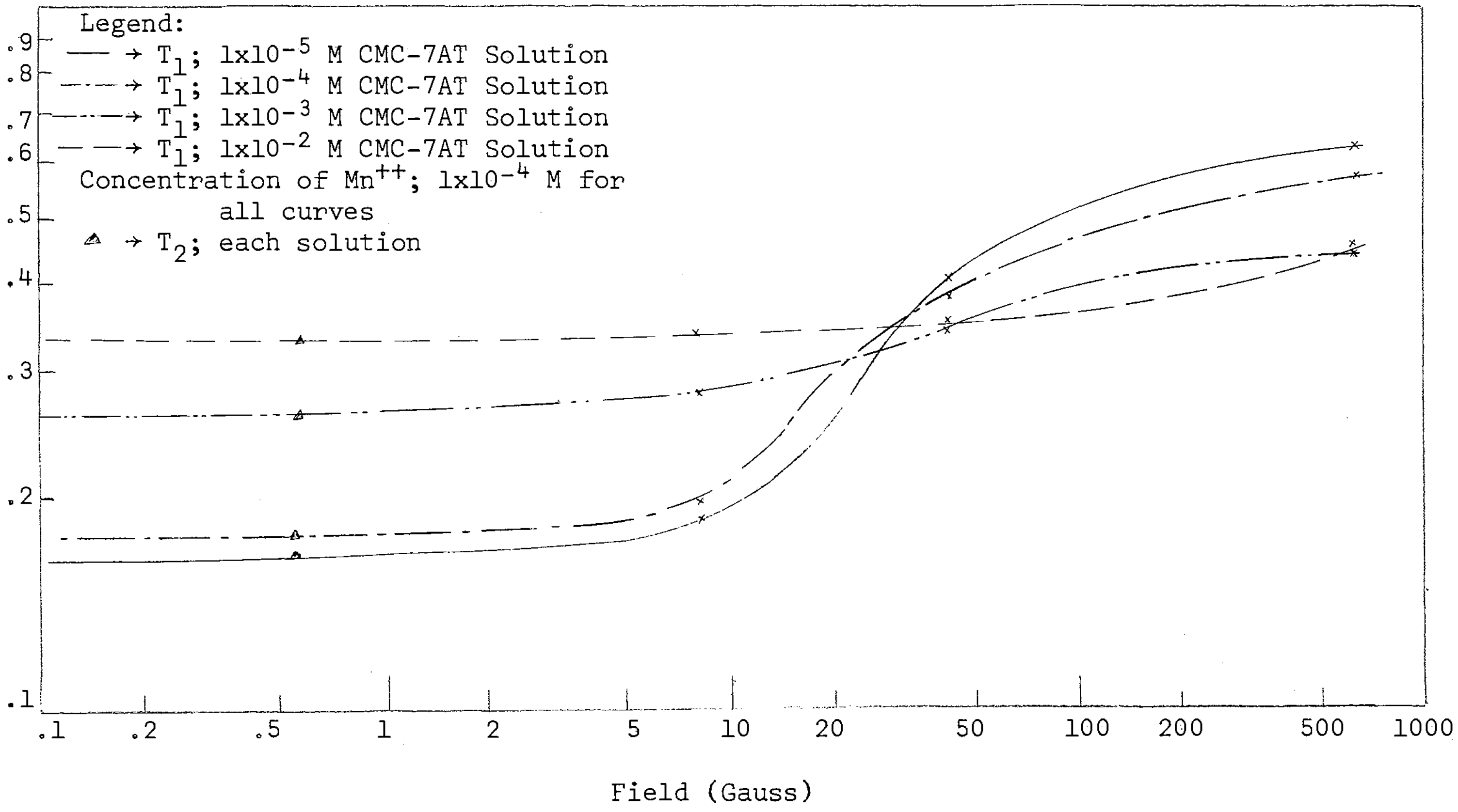

Figure 3. $T_{1,2}$ vs. Field for an Aqueous CMC-7AT and

Mn^{++} Solution

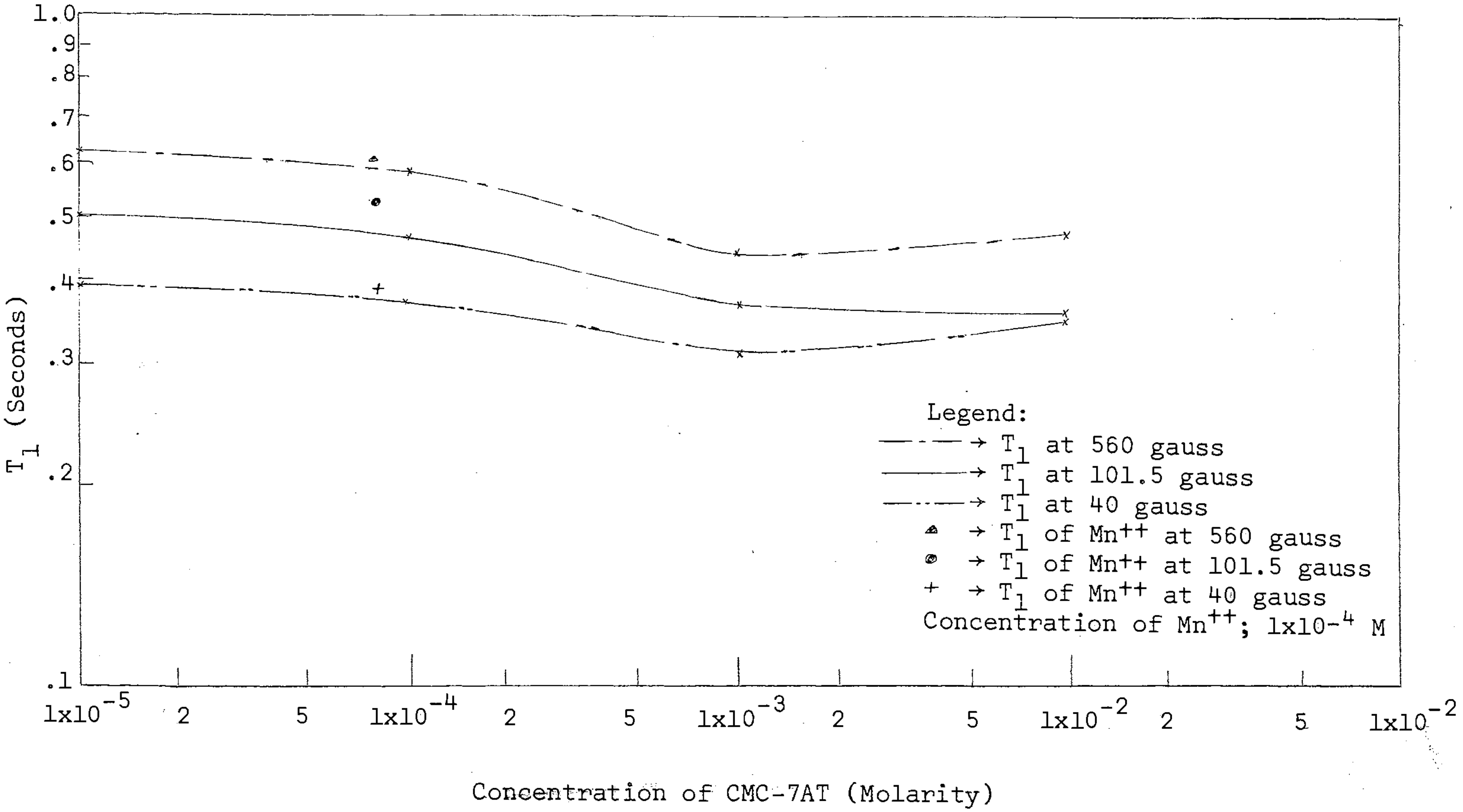

Figure 4. T_1 vs. Concentration of CMC-7AT at 25° C.

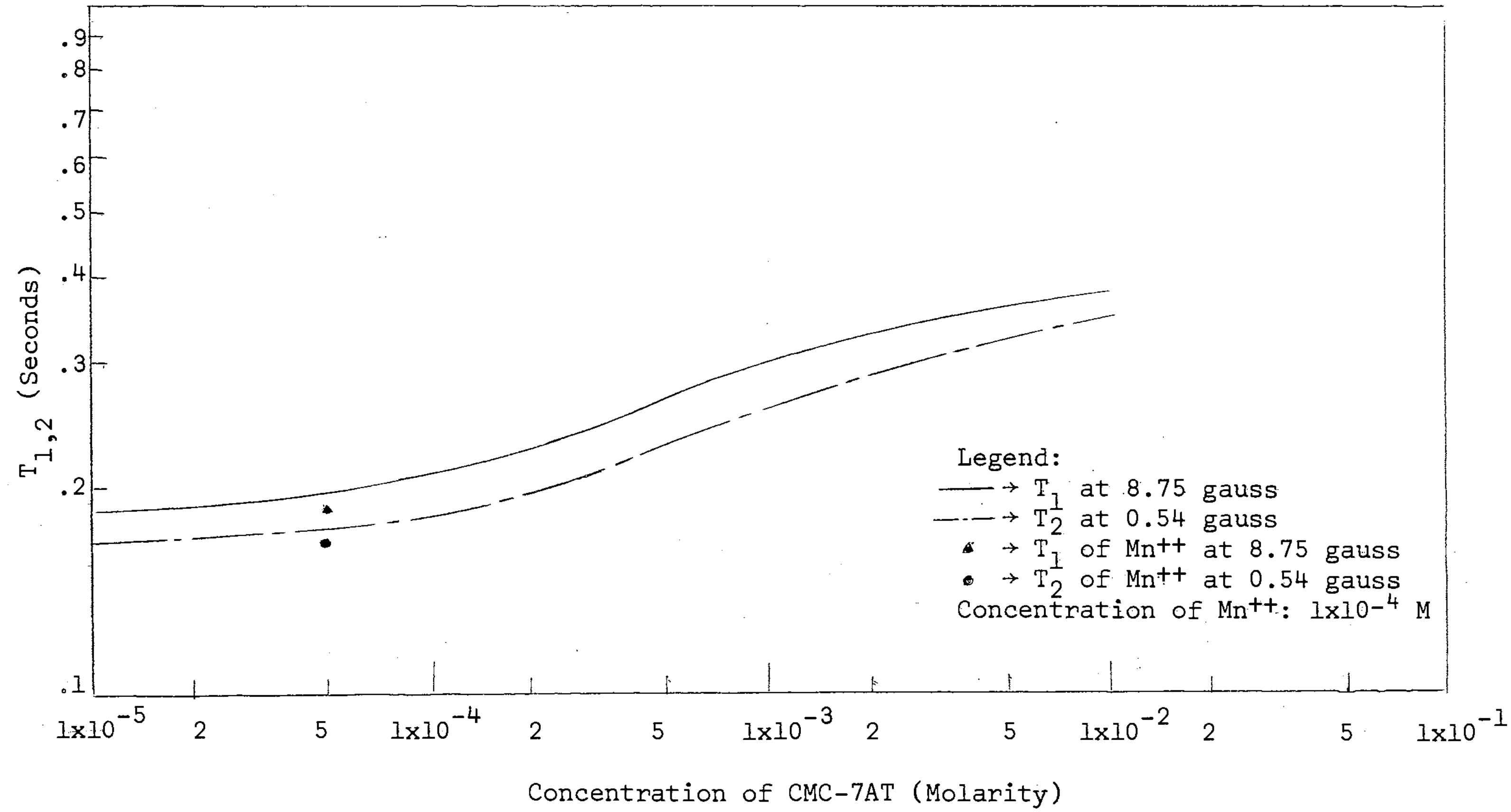

Figure 5. $T_{1,2}$ vs. Concentration of CMC-7AT at 25° C.

TABLE I

P- AMINOBENZOIC ACID AND Cu^{++}

Conc't. of P- Aminobenzoic Acid: 5×10^{-3} M

Conc't. of Cu^{++}: 3×10^{-3} M

	$T_{1,2}$ in Milsec.		
Field In Gauss	Raw Data	Corr. For H_2O	ϵ
535	264	285	0.99
101.5	240	257	1.02
39.6	230	246	1.06
8.05	234	252	1.01
T_2 @ 0.54	242	260	0.99

Conc't. of P-Aminobenzoic Acid: 3×10^{-3} M

Conc't. of Cu^{++}: 3×10^{-3} M

	$T_{1,2}$ in Milsec.		
Field In Gauss	Raw Data	Corr. For H_2O	ϵ
539	255	274	1.03
101.5	248	267	0.98
39.2	232	248	1.05
8.05	226	242	1.06
T_2 @ 0.54	244	262	0.99

TABLE I (Continued)

Conc't. of P-Aminobenzoic Acid: 1 x 10^{-3} M			
Conc't. of Cu^{++}: 3 x 10^{-3} M			
	$T_{1,2}$ in Milsec.		
Field In Gauss	Raw Data	Corr. For H_2O	ε
539	252	272	1.04
101.5	231	247	1.06
39.4	229	245	1.06
8.05	233	249	1.03
T_2 @ 0.54	243	260	0.99

TABLE II

METHIONINE AND Cu^{++}

Conc't. of Methionine: 3×10^{-3} M			
Conc't. of Cu^{++}: 3×10^{-3} M			
	$T_{1,2}$ in Milsec.		
Field In Gauss	Raw Data	Corr. For H_2O	ε
560	255	274	1.03
105	264	285	0.52
39.9	258	277	0.94
7.7	244	262	0.97
T_2 @ 0.54	270	292	0.88

Conc't. of Methionine: 1×10^{-2} M			
Conc't. of Cu^{++}: 3×10^{-3} M			
	$T_{1,2}$ in Milsec.		
Field In Gauss	Raw Data	Corr. For H_2O	ε
567	302	330	0.86
105	267	288	0.92
39.6	279	302	0.86
7.7	276	298	0.86
T_2 @ 0.54	285	209	0.84

TABLE II (Continued)

Conc't. of Methionine: 3×10^{-4} M			
Conc't. of Cu^{++}: 3×10^{-3} M			
	$T_{1,2}$ in Milsec.		
Field In Gauss	Raw Data	Corr. For H_2O	ϵ
560	276	298	0.95
105	225	239	1.10
39.9	238	255	1.02
7.7	241	258	0.99
T_2 @ 0.54	248	267	0.97

Conc't. of Methionine: 3×10^{-5} M			
Conc't. of Cu^{++}: 3×10^{-3} M			
	$T_{1,2}$ in Milsec.		
Field In Gauss	Raw Data	Corr. For H_2O	ϵ
570.5	245	263	1.07
105	272	294	0.89
39.9	229	245	1.06
7.7	238	255	1.00
T_2 @ 0.54	248	267	0.97

TABLE III

TYROSINE AND Cu^{++}

Conc't. of Tyrosine: 1 x 10^{-3} M			
Conc't. of Cu^{++}: 3 x 10^{-3} M			
	$T_{1,2}$ in Milsec.		
Field In Gauss	Raw Data	Corr. For H_2O	ϵ
546	246	264	1.07
101.5	233	249	1.05
40.7	232	248	1.05
8.05	229	245	1.04
T_2 @ 0.54	230	246	1.05

Conc't. of Tyrosine: 2 x 10^{-3} M			
Conc't. of Cu^{++}: 3 x 10^{-3} M			
	$T_{1,2}$ in Milsec.		
Field In Gauss	Raw Data	Corr. For H_2O	ϵ
546	276	298	0.95
101.5	251	270	0.97
40.7	245	263	0.99
8.05	246	264	0.97
T_2 @ 0.54	237	254	1.02

TABLE III (Continued)

Conc't. of Tyronsine: 1 x 10^{-4} M			
Conc't. of Cu^{++}: 3 x 10^{-3} M			
	$T_{1,2}$ in Milsec.		
Field In Gauss	Raw Data	Corr. For H_2O	ϵ
546	257	277	1.02
101.5	235	251	0.97
40.7	235	251	0.96
8.05	236	252	1.01
T_2 @ 0.54	235	251	0.96

TABLE IV

PYRIDINE AND Cu^{++}

Conc't. of Pyridine: 3×10^{-2} M			
Conc't. of Cu^{++}: 3×10^{-3} M	Conc't. of HCl: 2×10^{-2} M		
	$T_{1,2}$ in Milsec.		
Field In Gauss	Raw Data	Corr. For H_2O	ε
560			
101	424	280	0.60
41.3			
8.05	388	434	0.61
T_2 @ 0.54	391	437	0.62

Conc't. of Pyridine: 3×10^{-3} M			
Conc't. of Cu^{++}: 3×10^{-3} M	Conc't. of HCl: 2×10^{-2} M		
	$T_{1,2}$ in Milsec.		
Field In Gauss	Raw Data	Corr. For H_2O	ε
560	359	398	0.70
101	331	364	0.70
8.05			
T_2 @ 0.54	303	330	0.82

TABLE IV (Continued)

Conc't. of Pyridine: 3×10^{-3} M			
Conc't. of Cu^{++}: 3×10^{-3} M		Conc't. of HCl: 2×10^{-2} M	
	$T_{1,2}$ in Milsec.		
Field In Gauss	Raw Data	Corr. For H_2O	ε
567	269	290	0.97
101	274	296	0.97
40.9	257	277	1.02
8.05	252	271	0.97
T_2 @ 0.54	242	260	1.04

Conc't. of Pyridine: 1×10^{-3} M			
Conc't. of Cu^{++}: 3×10^{-3} M		Conc't. of HCl: $2 X 10^{-2}$ M	
	$T_{1,2}$ in Milsec.		
Field In Gauss	Raw Data	Corr. For H_2O	ε
567	233	249	1.12
101	255	274	1.05
40.9	250	268	1.05
8.05	233	249	1.06
T_2 @ 0.54	221	236	1.15

TABLE IV (Continued)

Conc't. of Pyridine: 3×10^{-4} M			
Conc't. of Cu^{++}: 3×10^{-3} M		Conc't. of HCl: 2×10^{-2} M	
	$T_{1,2}$ in Milsec.		
Field In Gauss	Raw Data	Corr. For H_2O	ϵ
546	246	264	1.06
101	233	249	1.16
40.7	232	248	1.14
8.05	229	245	1.07
T_2 @ 0.54	230	246	1.10

TABLE V

PYRIDINE, Cu^{++}, AND PERCHLORIC ACID

Conc't. of Pyridine: 9×10^{-3} M

Conc't. of Cu^{++}: 3×10^{-3} M   Conc't. of Perchloric Acid: 1×10^{-2} M

	$T_{1,2}$ in Milsec.		
Field In Gauss	Raw Data	Corr. For H_2O	ϵ
560	260	280	0.97
101		?	
39.2	247	265	1.05
8.05	229	244	1.02
T_2 @ 0.54	241	259	0.98

Conc't. of Pyridine: 1.2×10^{-3} M

Conc't. of Cu^{++}: 3×10^{-3} M   Conc't. of Perchloric Acid: 1×10^{-2} M

	$T_{1,2}$ in Milsec.		
Field In Gauss	Raw Data	Corr. For H_2O	ϵ
560	251	270	1.00
101.5	248	267	1.00
39.2	250	269	1.01
8.05	226	241	1.03
T_2 @ 0.54	239	256	0.99

TABLE V (Continued)

Conc't. of Pyridine: 3×10^{-3} M			
Conc't. of Cu^{++}: 3×10^{-3} M		Conc't. of Perchloric Acid: 1×10^{-2} M	
	$T_{1,2}$ in Milsec.		
Field In Gauss	Raw Data	Corr. For H_2O	ε
560	247	265	1.02
108.5	246	264	1.01
39.2	245	263	1.04
8.05	227	243	1.02
T_2 @ 0.54	236	252	1.01

TABLE VI

CMC-7AT AND Mn^{++}

Conc't. of CMC-7AT: 1×10^{-2} M				
Conc't. of Mn^{++}: 1×10^{-4} M				
	$T_{1,2}$ in Milsec.			
Field In Gauss	Raw Data	Corr. For H_2O	ε	K_a
560	452	516	1.50	1.5×10^3
101.5	376	418	1.54	9.3×10^2
39.2	373	415	1.10	4.2×10^2
8.05	351	388	0.48	
T_2 @ 0.54	328	360	0.48	

Conc't. of CMC-7AT: 1×10^{-3} M				
Conc't. of Mn^{++}: 1×10^{-4} M				
	$T_{1,2}$ in Milsec.			
Field In Gauss	Raw Data	Corr. For H_2O	ε	K_a
560	443	503	1.54	1.1×10^4
101.5	367	408	1.58	8.4×10^3
39.2	323	356	1.28	2.9×10^3
8.05	275	297	0.63	
T_2 @ 0.54	258	278	0.62	

TABLE VI (Continued)

Conc't. of CMC-7AT: 1 x 10^{-4} M

Conc't. of Mn++: 2 x 10^{-4} M

	$T_{1,2}$ in Milsec.			
Field In Gauss	Raw Data	Corr. For H_2O	ε	K_a
560	575	682	1.13	1.1 x 10^3
101.5	474	545	1.18	2.4 x 10^4
39.2	380	424	1.12	9.2 x 10^3
8.05	195	206	0.90	
T_2 @ 0.54	175	184	0.76	

Conc't. of CMC-7AT: 1 x 10^{-5} M

Conc't. of Mn^{++}: 1 x 10^{-4} M

	$T_{1,2}$ in Milsec.			
Field In Gauss	Raw Data	Corr. For H_2O	ε	K_a
560	617	743	1.05	3.9 x 10^4
101.5	519	604	1.06	2.4 x 10^4
9.2	405	456	1.00	3.3 x 10^2
8.05	180	189	0.98	
T_2 @ 0.54	167	176	0.98	

TABLE VI (Continued)

Conc't. of CMC-7AT: 1 x 10^{-3} M			
Conc't. of Mn^{++}: 0.0 M			
	$T_{1,2}$ in Sec.		
Field in Gauss	Raw Data	Corr. For H_2O	
528.5	3.70	0.00	
98.0	3.69	0.00	
39.9	3.66	0.00	
7.70	3.66	0.00	
T_2 @ 0.54	0.88	0.00	

TABLE VII

Cu^{++} AND Mn^{++}

Conc't. of Cu^{++}: 3×10^{-3} M

	$T_{1,2}$ in Milsec.	
Field In Gauss	Raw Data	Corr. For H_2O
557	261	282
101.5	244	262
39.9	243	260
8.05	238	255
T_2 @ 0.54	242	258

Conc't. of Cu^{++}: 3×10^{-3} M

Conc't. of HCl: 2×10^{-2} M

	$T_{1,2}$ in Milsec.	
Field In Gauss	Raw Data	Corr. For H_2O
573	260	280
101.5	269	288
41.1	261	282
8.05	245	263
T_2 @ 0.54	252	272

TABLE VII (Continued)

Conc't. of Cu^{++}: 3×10^{-3} M		
Conc't. of Perchloric Acid: 1×10^{-3} M		
	$T_{1,2}$ in Milsec.	
Field In Gauss	Raw Data	Corr. For H_2O
562	251	270
101.5	248	267
39.5	253	272
8.05	232	248
T_2 @ 0.54	237	254

Conc't. of Mn^{++}: 1×10^{-4} M		
	$T_{1,2}$ in Milsec.	
Field In Gauss	Raw Data	Corr. For H_2O
560	636	772
101.5	546	643
39.2	407	457
8.05	177	186
T_2 @ 0.54	164	172

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