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THE EFFECT OF Cl^- AND SO_4^{-2} ON THE PARAMAGNETIC RESONANCE LINE WIDTH OF Mn^{+2} IN AQUEOUS SOLUTION AND THE RATES OF FORMATION OF THE COMPLEX IONS

Robert G. Hayes and Rollie J. Myers

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I. Introduction

Solutions of manganous ion were among the first aqueous solutions of transition metal ions in which electron paramagnetic resonance (EPR) was detected.[1] The spectrum of Mn^{+2} in dilute solution at room temperature consists of six lines, each about 30 oe wide, and each separated by 95 oe. These six lines arise from interaction of the electronic spin with the nuclear moment of Mn^{55} $(I = \frac{5}{2})$.

More careful examination of the spectrum of Mn^{+2} shows that the six lines do not all have the same width. The narrowest line at 9000 mc/sec is the fourth from the low field end of the spectrum. The third and fifth lines are of roughly the same width and somewhat wider than the fourth, and the second and sixth lines are still wider. The first line is widest. This variation in width was explained by Tinkham.[2] He showed that second order effects were appreciable in the spectrum at 9000 mc. These second order effects, which arise from the off-diagonal terms of the isotropic hyperfine coupling, split the five transitions (superimposed in the strong field representation) which compose each of the six lines. This splitting varies from one hyperfine component to another and causes the differences in width. The analysis shows that the narrowest line, which corresponds to $M_I = +\frac{1}{2}$, is essentially unsplit at 9000 mc. Thus this line is the only one suitable for studies of magnetic relaxation in Mn^{+2}.

The EPR line widths of Mn^{+2} in aqueous solution have been studies by several workers. One of the early studies was made by McGarvey,[3] who observed the linewidth of $MnCl_2$ solutions at room temperature and 9000 mc/sec. He tried to explain the observed width as the result of imperfect rotational averaging of some fixed zero field splitting of the ion. However, Bloembergen and Morgan[4] have shown convincingly that the mechanism of relaxation of Mn^{+2} does not involve rotational averaging by studying the effect of Mn^{+2} on the relaxation of the protons in H_2O. They propose instead that the relaxation is due to a fluctuating zero field splitting caused by water molecules darting in and out of the vicinity of the ion. They show that good agreement with experiment can be obtained by using the correlation times deduced from their experiments with proton relaxation and a mean squared zero field splitting equal to the static splitting observed in crystals. More recently Nolle and Morgan[5] have measured the line width of the $M_I = + \frac{1}{2}$ line in dilute solutions of $Mn(ClO_4)_2$ as a function of temperature and have shown that the temperature and frequency dependence agrees roughly with that deduced from proton relaxation measurements. It still remains for detailed calculations to be done for this model in order to establish its complete validity. We shall not be concerned with this difficult question but shall only consider the effects of anions on the linewidth of Mn^{+2}. We shall assume that the behavior of dilute $Mn(ClO_4)_2$ solutions represents the behavior of Mn^{+2} unperturbed by anion effects, since changing the concentration of ClO_4^- in these solutions does not affect the line width appreciably.

There appears to be but one previous published observation of the effect of a diamagnetic anion on the relaxation of Mn^{+2}. Kozyrev and his associates[6] have studied the line width of $MnCl_2$ solutions between room temperature and about 200°C and have observed effects similar to those we report below. Unfortunately, they musunderstood their results, assuming the behavior they observed to be intrinsic to the Mn^{+2} rather than the chloride ion that was also in the solution.

II. Experimental

Spectra were taken with a conventional X-band EPR apparatus employing 100 cps magnetic field modulation. Elevated temperatures were obtained by passing hot air over the sample which was contained in a quartz dewar tube inserted in the cavity. Temperatures were measured using a very fine Cu-constantin thermocouple wrapped around a glass rod which was sealed to the sample tubes. Because of local temperature fluctuations and because the thermocouple was not directly attached to the samples, the measured temperatures may be in error by as much as 2° at the upper end of our temperature range. Samples were at first contained in heavy walled tubes but it was later found that ordinary melting point capillary tubing served as well, so this was used instead. Magnetic field measurements were made with a proton resonance probe and a frequency counter. Reported line widths refer to full width at points of maximum slope. The symbol ΔH will be used for this quantity.

III. $Mn(ClO_4)_2$ Solutions

The line widths of several $Mn(ClO_4)_2$ solutions were studied from 20° to 200°. In the range from 20° to 100° no difference at all could be observed between a 0.05 M and a 0.01 M $Mn(ClO_4)_2$ solution. Above 100°C the 0.05 M solution had widths which differed by as large as 0.5 oe. from the more dilute ones, but the trend with dilution was always small and the most dilute solution did not always give the narrowest line width at all temperatures. Since we primarily wanted to compared the much larger effect of Cl^- and SO_4^{-2} ions we have adopted the 0.05 M $Mn(ClO_4)_2$ as a reference. In Fig. 1 we show the variation of line width of this solution with temperature.

IV. Effect of Chloride

In Fig. 1 the effect of adding NaCl to a 0.05 M $Mn(ClO_4)_2$ solution is shown. In the concentration range shown the effect of added Cl^- below 80° was always less than 1 oe and it is omitted from this figure. Above 80° the widths of the Cl^- containing solutions are much greater and they change rapidly with temperature. The excess width of the Cl^- containing solutions over that of the pure ClO_4^- solution is nearly but not exactly proportional to the Cl^- concentration. This is clearly indicated by the 0.05 M $MnCl_2$ curve shown in Fig. 1. In order to illustrate both the effects of Cl^- and of temperature the excess widths divided by the Cl^- concentrations for all the Cl^- solutions run are given in Fig. 2.

The straight line in Fig. 2 was drawn as the best line through the points containing 0.1 M ClO_4^- but it was also drawn parallel to the 0.05 M $MnCl_2$ points. It can be seen from this figure that while ionic strength effects seem to enter and the excess width is not exactly a linear function of the Cl^- concentration, these deviations are secondary to the overall trend with temperature and Cl^- concentration.

V. Effect of Sulfate

Figure 3 displays the results obtained from several sulfate systems. As can be seen, the effects of the SO_4^{-2} are more complex than those of Cl^-. For one thing, there is a large contribution to the width at all temperatures due to the presence of SO_4^{-2}. For another, the effect of SO_4^{-2} is not even nearly proportional to the concentration of the ion.

VI. Discussion

It is quite apparent from the Cl^- and SO_4^{-2} data that complex formation is the source of the excess line width. The qualitative difference between the room temperature behavior of Cl^- and SO_4^{-2} is readily explained by the expected size of the equilibrium constants for complex formation with a divalent ion like Mn^{+2}. The expected value for the equilibrium constant[7] at 20°C and low ionic strength for the formation of a $MnCl^+$ complex is about 0.1 M^{-1} and for $MnSO_4$ complex it is about 100 M^{-1}. In the anion concentrations shown in Fig. 1 and Fig. 3 the Mn^{+2} is not appreciably complexed by Cl^- but some SO_4^{-2} complex is to be expected.

Several additional details must be considered. One must consider both "inner-sphere" and "outer-sphere" complexes and the rates of formation of these complexes. This is particularly evident in the SO_4^{-2} case where the opposite effects on line width are observed in the low and high temperature regions.

Pearson and Buch[8] have considered the effect of the rates of complex formation upon EPR line widths. In most of the cases that they considered they assume that the line width was primarily determined by the rate of formation of a second coordination sphere complex, and this is a reasonable assumption for their systems. In the case of Cl^- we shall show that the line width is determined by a first coordination sphere complex while the SO_4^{-2} line widths are affected by both rates depending upon the temperature. In the development of our theory we shall use a notation, in as much as is possible, which is consistent with Pearson and Buch.

Before these results can be interpreted in terms of interactions between Mn^{+2} and the anions in the solution one must convert the measured line widths in magnetic field units into transverse relaxation times, T_2. The relationship between ΔH and T_2 depends, as is well known, on the shape of the line. We shall assume this to be Lorentzian, an assumption which is consistent with the model we propose below. Under this assumption T_2 and ΔH are related by the expression $T_2 \Delta H = h(\sqrt{3}\ \pi g\beta)^{-1}$. Thus a width of 1 oe corresponds to $T_2 = 6.55 \times 10^{-8}$ sec.

Some interaction between a Mn^{+2} ion and an anion presumably exists at all distances of separation between the two but we shall assume that this does not become significantly large until the anion occupies a coordination sphere about the Mn^{+2}. We shall assume that the first important coordination position for relaxation is when the anion enters the second coordination sphere. Thus, we shall consider three manganous species in solution. These are manganous ions with no anion in the first or second coordination sphere, manganous ions with an anion in the second coordination sphere and manganous ions with an anion in the first coordination sphere. We shall call them Mn^{+2}, $Mn^{+2}\ H_2OX^{-n}$, and $Mn^{+2}\ X^{-n}$ respectively, or alternately, species a, b, and c respectively.

We define the following rate and equilibrium constants:

$$Mn^{+2} + X^{-n} \underset{k_{ba}}{\overset{k_{ab}}{\rightleftharpoons}} Mn^{+2}\ H_2O\ X^{-n} \qquad (1)$$

$$Mn^{+2}\ H_2O\ X^{-n} \underset{k_{cb}}{\overset{k_{bc}}{\rightleftharpoons}} Mn^{+2}\ X^{-n} \qquad (2)$$

$$K_{ab} = \frac{k_{ab}}{k_{ba}}\ , \qquad K_{bc} = \frac{k_{bc}}{k_{cb}} \qquad (3)$$

$$\tau_a = \frac{1}{k_{ab}[X^{-n}]}\ , \qquad \tau_{ba} = \frac{1}{k_{ba}} \qquad (4)$$

$$\tau_{bc} = \frac{1}{k_{bc}}\ , \ \tau_c = \frac{1}{k_{cb}}\ . \qquad (5)$$

Let T_{2a} be the transverse relaxation time of the Mn^{+2} species. This will be identified with the relaxation times observed for $Mn(ClO_4)_2$ solutions. Let T_{2b} and T_{2c} be the relaxation times of Mn^{+2} H_2O X^{-n} and Mn^{+2} X^{-n}, respectively. These are the EPR relaxation times that would be observed if the manganous were present in the indicated forms at all times.

If we consider for the moment only the first two species a and b there are two possible extreme circumstances not specifically covered by Pearson and Buch. If $\tau_a \gg T_{2a}$ and $\tau_{ba} \gg T_{2b}$ then the equilibrium between these two species can be considered as frozen and the EPR spectrum will be a simple superposition of the individual spectra of the two separate species. Pearson and Buch's equation (5) can not be reduced to this result because of the approximation of Lorentzian form in this equation. For slow exchange the observed absorption would not be Lorentzian since the sum of two Lorentzian absorption curves is not itself of the Lorentzian form, even if $\omega_a = \omega_b$. If one utilizes a derivative method for line width determination it can be readily determined that the ΔH value is dominated by the species with the smaller line width. Since Mn^{+2} is expected to have the largest value of T_2, e.g. $T_{2a} > T_{2b} > T_{2c}$, a relatively large amount of Mn^{+2} H_2O X^{-n} or Mn^{+2} X^{-n} must be formed under slow exchange before the ΔH values could be expected to approach their line widths. For example, if two species a and b are present in equal amounts and $T_{2b} = T_{2a}/10$ slow exchange would give a ΔH value which would be increased by only 0.1% over that for species a alone.

It is quite probable that at low temperatures the Mn^{+2} X^{-n} species is exchanged with Mn^{+2} and Mn^{+2} H_2O X^{-n} relatively slowly and that the values of T_{2c} are relatively small. In this case, the observed line width will almost entirely be determined by the Mn^{+2} and Mn^{+2} H_2O X^{-n}. At higher temperatures this may not be true.

If on the other hand, $\tau_a \ll T_{2a}$ and $\tau_{ba} \ll T_{2b}$ an exact Lorentzian form is to be expected and we have the well known result for fast exchange

$$1/T_2 = /P_aT_{2a} + P_b/T_{2b} \qquad (6)$$

where P_a and P_b are the respective mole fractions. If $T_{2a} > T_{2b}$ and $P_a > P_b$ a useful form of Eq. (6) is

$$1/T_2 - 1/T_{2a} = P_aK_{ab}\ [X^{-n}]\ (1/T_{2b} - 1/T_{2a})\ . \qquad (7)$$

This equation is similar to Pearson and Buch's Eq. (8) for the case $\tau_{ba} < T_{2b}$.

In order to make quantitative use of the chloride and sulfate data it is necessary to consider the primary sources of line width. Since the line width is not only determined by the T_2 values alone but also by the τ values it is necessary to make estimates of both of these values. In Table I we show such a set of estimates. The anion concentration was assumed to be 0.05 M in all cases and ionic strength effects have been neglected in making these estimates.

Chloride Ion - The estimates of τ_a were made by assuming that k_{ab} is a diffusion controlled reaction.[8] We estimate at 20°C and 160°C respectively that k_{ab} varies from 2×10^{10} to $2 \times 10^{11}\ M^{-1}\ sec^{-1}$. The higher value at 160°C is due to the well known decrease in both the viscosity and dielectric constant for water at higher temperatures. From Table I it can be seen that $\tau_a < T_{2a}$ particularly at the higher temperatures. Since τ_a would increase as the anion concentration is lowered the condition $\tau_a < T_{2a}$ would not be expected at very low concentrations. Above 100°C and at our Cl^- concentration we do have the case where $\tau_a < T_{2a}$.

The equilibrium constant K_{ab} should be small and the values of τ_{ba} were obtained assuming that $K_{ab} = 10^{-1}\ M^{-1}$ at all temperatures. It is possible that K_{ab} is smaller than this at low temperatures and high ionic strengths. The relaxation time T_{2b} cannot be measured, but the contribution of an anion in the second coordination sphere to the D term in the spin Hamiltonian should be similar to that estimated[4] for Mn^{+2} and that found for crystals[9] containing hydrated manganous ion. The correlation time for $Mn^{+2}\ H_2O\ X^{-n}$ should be close to that expected for tumbling so that at 20°C we would estimate that $T_{2a}/T_{2b} \sim 10$. At 160°C the higher activation energy for tumbling might make T_{2a} and T_{2b} fairly close in value and T_{2b} should be no smaller than 10^{-9} sec at the higher temperatures.

The lifetime τ_{ba} is very small indeed and as a very good approximation $\tau_{ba} < T_{2b}$ at nearly all temperatures. Over most of the temperature region in Fig. 1, Eq. (7) should apply to the Mn^{+2} and $Mn^{+2}\ H_2OCl^-$ species. Since we find that chloride causes only a 1% increase in line width below 80°C and at 0.1 M we can conclude from Eq. (7) that $K_{ab}/T_{2b} \approx 10^{-1}/T_{2a}$ under these conditions. This result is very close to our estimates as it indicates the $K_{ab} \leq 10^{-1}\ M^{-1}$ at 0.1 M and below 80°C.

It is not very likely that Eq. (7) would predict a large increase in line width with increasing temperature. The enthalpy associated with K_{ab} should nearly cancel the activation energy associated with T_{2b} since they are both expected to be in the range 3 to 5 Kcal/mole. The dramatic increase in line width in Fig. 1 and its 9.35 Kcal/mole activation energy cannot arise from conditions of fast exchange. Since the first coordination sphere species contributes very little to the line width at low temperatures we are led to assume that the increase at high temperatures is associated with this species. If we have the conditions with $\tau_c < T_{2c}$ all three species would be in fast exchange and the 9.35 Kcal/mole cannot be explained. But it is clear that τ_c must decrease with increasing temperature so that the first coordination sphere species can contribute to the line width.

If we have the condition where $\tau_c \gg T_{2c}$ then everytime a first coordination sphere complex is formed it results in relaxation. Under these conditions a variety of equations can be obtained from Pearson and Buch's equation (7). With the conditions $\tau_a < T_{2a}$, $\tau_{ba} < T_{2b}$, $\tau_{bc} < T_{2b}$ and $\tau_c > T_{2c}$ one can expect that

$$1/T_2 = P_a/T_{2a} + P_b/\tau_{bc} \tag{8}$$

or

$$1/T_2 - 1/T_{2a} = P_a K_{ab}\ [\mathrm{Cl}^-] \left[k_{bc} - (1 + K_{bc})/T_{2a}\right] \tag{9}$$

For chloride complexes under our conditions P_a is very close to unity and $k_{bc} > 1 + K_{bc}/T_{2a}$ so that

$$1/T_2 - 1/T_{2a} = K_{ab}\ k_{bc}\ [\mathrm{Cl}^-]. \tag{10}$$

From the data in Fig. 2 at 160°C excess width/$[\mathrm{Cl}^-]$ = 130 oe M^{-1} so that $K_{ab}\ k_{bc} = 2.0 \times 10^{-9}$ $\sec^{-1}$ M^{-1} at 160°C and 1.5×10^{7} $\sec^{-1}$ M^{-1} at 25°C. The values of τ_c and τ_{bc} in Table I were calculated assuming that $K_{ab} = 10^{-1}$ M^{-1} at 20° and 1 M^{-1} at 160°C.[10] The values of T_{2c} were estimated assuming[4] that D^2 for $\mathrm{Mn}^{+2}\ X^{-n}$ were ten times those previously estimated for $\mathrm{Mn}^{+2}\ H_2O\ X^{-n}$. It can be seen from Table I that the estimated times are in reasonable agreement with the assumptions which are made in order to derive Eq. (10).

It is possible that the very act of removal of water from the first coordination sphere and its replacement by Cl^- would lead to spin relaxation. If this were the case then it would not be necessary in Eq. (8) to have any relationship between τ_c and T_{2c}. The consistency of our values for $K_{ab}\ k_{bc}$ with other data will be discussed later.

Sulfate Ion - The values in Table I for the sulfate ion case were estimated in much the same way as the chloride were. Eigen and Tamm[11] for both chloride and sulfate. The values of τ_{ba} were calculated assuming $K_{ab} = 10\ M^{-1}$ at all temperatures. The data of Eigen and Tamm were used at 20°C to determine τ_{bc} and τ_c and the 160°C values were estimated by assuming an activation energy for k_{bc} of 9.0 Kcal/mole still keeping[11] $K_{bc} = 0.2$ at all temperatures.

A graph of the excess width for 0.05 M $Mn(ClO_4)_2$ solutions with added Na_2SO_4 is shown in Fig. 4. At the lower temperatures the excess width is nearly a linear function of the $[SO_4^{-2}]$ and it is not very dependent upon temperature. Above 100°C, as can also be seen in Fig. 3, the line width increases with temperature as it does in the chloride case but at the very highest temperatures added sulfate above the stoichiometric amount has little effect.

In the 20-80°C range we should be able to apply Eq. (7). This equation predicts an excess width which is nearly independent of temperature and if K_{ab} is small enough the excess width should also be linear in added sulfate. The near linearity in added sulfate requires a K_{ab} values as low as 1 M^{-1}. Ionic strength effects make this low a value possible. The initial slope of the 20-80°C curve in Fig. 4 is 100 oe M^{-1} and Eq. (7) would predict that $T_{2b}/K_{ab} = 6 \times 10^{-10}$ M sec. This is in good agreement with our estimates in Table I if K_{ab} is close to the value of 1 M^{-1} at the low temperatures our ionic strength.

In Fig. 4 at 160°C it is clear that $K_{ab} \approx 100\ M^{-1}$ so that P_b is a linear function of the added sulfate only up to the stoichiometric requirement. If we apply Eq. (8) to the total line width observed for the 0.1 M sulfate data at 160°C with $P_a = 0$ and $P_b = 1$ then we obtain $\tau_{bc} = 2 \times 10^{-9}$ sec. Some other runs[12] were also made on a 0.005 M $MnSO_4$ solution. If we apply Eq. (10) to the

160°C excess line width of 10 oe obtained for 0.005 $\underline{M}$ $MnSO_4$ we find that τ_{bc}/K_{ab} $[SO_4^{-2}] = 2 \times 10^{-9}$ sec. Since the product of K_{ab} $[SO_4^{-2}]$ is probably close to unity under the conditions of 0.005 $\underline{M}$ $MnSO_4$ the agreement is very satisfactory considering the large difference in ionic strength.

The activation energy that is found for the excess width of the 0.005 $\underline{M}$ $MnSO_4$ data[12] is 4.8 Kcal/mole. On the other hand the total line width of the 0.1 $\underline{M}$ Na_2SO_4 data gives only about a 2.8 Kcal/mole activation energy. These two values give at 20°C τ_{bc}/K_{ab} $[SO_4^{-2}] = 2 \times 10^{-8}$ and $\tau_{bc} = 1 \times 10^{-8}$ sec. Both of these estimates are at least a factor of ten shorter than the 2×10^{-7} sec value for τ_{bc} of Eigen and Tamm.[11] In Table I it took a 9.0 Kcal/mole activation energy to correct their 20°C value to our observed 160°C lifetime. It is to be expected that the quantity τ_{bc} K_{ab} $[SO_4^{-2}]$ should have a larger activation energy than does τ_{bc}. The 2 Kcal mole difference in activation is too small for K_{ab} alone since the low and high temperature data require a variation in K_{ab} such that nearly an 8 Kcal/mole difference should be expected. It is clear however that the $[SO_4^{-2}]$ is not really constant even in 0.1 $\underline{M}$ Na_2SO_4. Further data will have to be obtained in solutions with more nearly constant ionic strength.

VII. Comparison and Conclusion

From the chloride data we were able to evaluate the quantity K_{ab} k_{bc} and its combined activation energy. Since we can only make estimates for K_{ab} it is not possible to evaluate the rate constant k_{bc} with accuracy. The line width increase at low temperatures indicate that $K_{ab} \leq 10^{-1}$ M^{-1}. However, the lifetimes τ_{ba} which are calculated in Table I are so small that a value for K_{ab} less than $10^{-1}M^{-1}$ would make our two-step complex model unrealistic. On basis of our data we must assume at room temperature that $K_{ab} = 10^{-1}M^{-1}$.

The change in enthalpy associated with K_{ab} is most certainly positive and it should be equivalent to an activation energy of about 3 Kcal/mole. If we assume this value than $k_{bc} = 1.5 \times 10^{8}$ sec^{-1} at 25°C and its activation energy is about 6 Kcal/mole.

Without considering the details of the process whereby the chloride ion moves from the second to the first coordination, it would appear that out value for k_{bc} is a reasonable one. This value and its activation energy yield a frequency factor equal to about 10^{12} sec^{-1}, and this is reasonable for a unimolecular reaction. The lifetime of the water molecules in the first coordination sphere of Mn^{+2} has been rather accurately determined.[4,13] Near room temperature this value is 3×10^{-8} sec and its activation energy is 8.1 Kcal/mole. This lifetime is about 5 times longer than our room temperature estimate for τ_{bc} and at 160°C the extrapolated values for the water lifetime would be very close to our estimates for τ_{bc}. The mechanisms for the replacement of a first coordination sphere water molecule by a chloride ion in the second coordination sphere or by a water molecule are most probably very similar. Our data indicate that chloride ion is only slightly faster than water in this replacement process. Tentative data for bromide ion and iodide ion also indicate similar rates of replacement. Further work on these ions and on chloride ion under condition of constant ionic strength is being done and such data should be very useful for a consideration of the mechanism of these reactions.

Our extrapolated value for τ_{bc} at room temperature for the sulfate system is about a factor of ten shorter than that determined by Eigen and Tamm.[11] In light of the complications of the sulfate system we must consider this as satisfactory agreement. Further work on the sulfate system with closely controlled ionic strength conditions should help classify this more complicated system.

VIII Acknowledgements

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Table I

Estimated Relaxation and Lifetimes[(a)]

	20°	160°	20°	160°
τ_a	1×10^{-9}	1×10^{-10}	1×10^{-9}	1×10^{-10}
T_{2a}	3×10^{-9}	8×10^{-9}	3×10^{-9}	8×10^{-9}
τ_{ba}	5×10^{-12}	5×10^{-13}	5×10^{-10}	5×10^{-11}
T_{2b}	$\sim 10^{-10}$	$\sim 10^{-9}$	$\sim 10^{-10}$	$\sim 10^{-9}$
τ_{bc}	7×10^{-9}	5×10^{-10}	2×10^{-7} (b)	2×10^{-9}
τ_c	7×10^{-9}	5×10^{-10}	4×10^{-8} (b)	4×10^{-10}
T_{2c}	$\sim 10^{-11}$	$\sim 10^{-10}$	$\sim 10^{-11}$	$\sim 10^{-10}$

(a) Times are in seconds and they are estimated for 0.05 M solutions of anion with additional assumptions given in the text.

(b) Value from Ref. (11) - our value is about a factor of ten smaller than this.

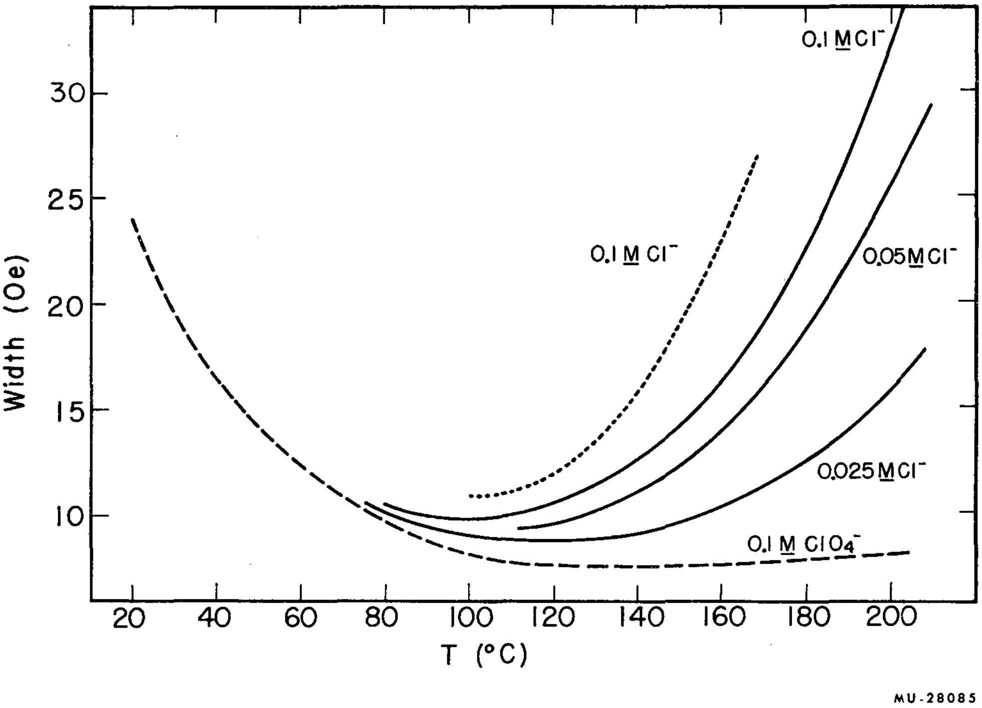
Figure Captions

Figure 1. The solid lines are a summary of the effect of added NaCl on the $M_I = +\frac{1}{2}$ component of 0.05$\underline{M}$ $Mn(ClO_4)_2$. The dashed curve is 0.05$\underline{M}$ $Mu(ClO_4)_2$ without added salt. The dotted curve is 0.05$\underline{M}$ Mn Cl_2.

Figure 2. The line drawn in this plot corresponds to an activation energy of 9.35 Kcal mole^{-1}. The points correspond to NaCl added to 0.05$\underline{M}$ $Mn(ClO_4)_2$ in the amount: ▨ 0.01$\underline{M}$, △ 0.025$\underline{M}$, □ 0.03$\underline{M}$, ⊖ 0.05$\underline{M}$, ◉ 0.1$\underline{M}$. The points ▲ correspond to 0.05$\underline{M}$ $MnCl_2$ and the points ⊖ to a solution 0.025$\underline{M}$ $Mn(ClO_4)_2$ with 0.05$\underline{M}$ added NaCl.

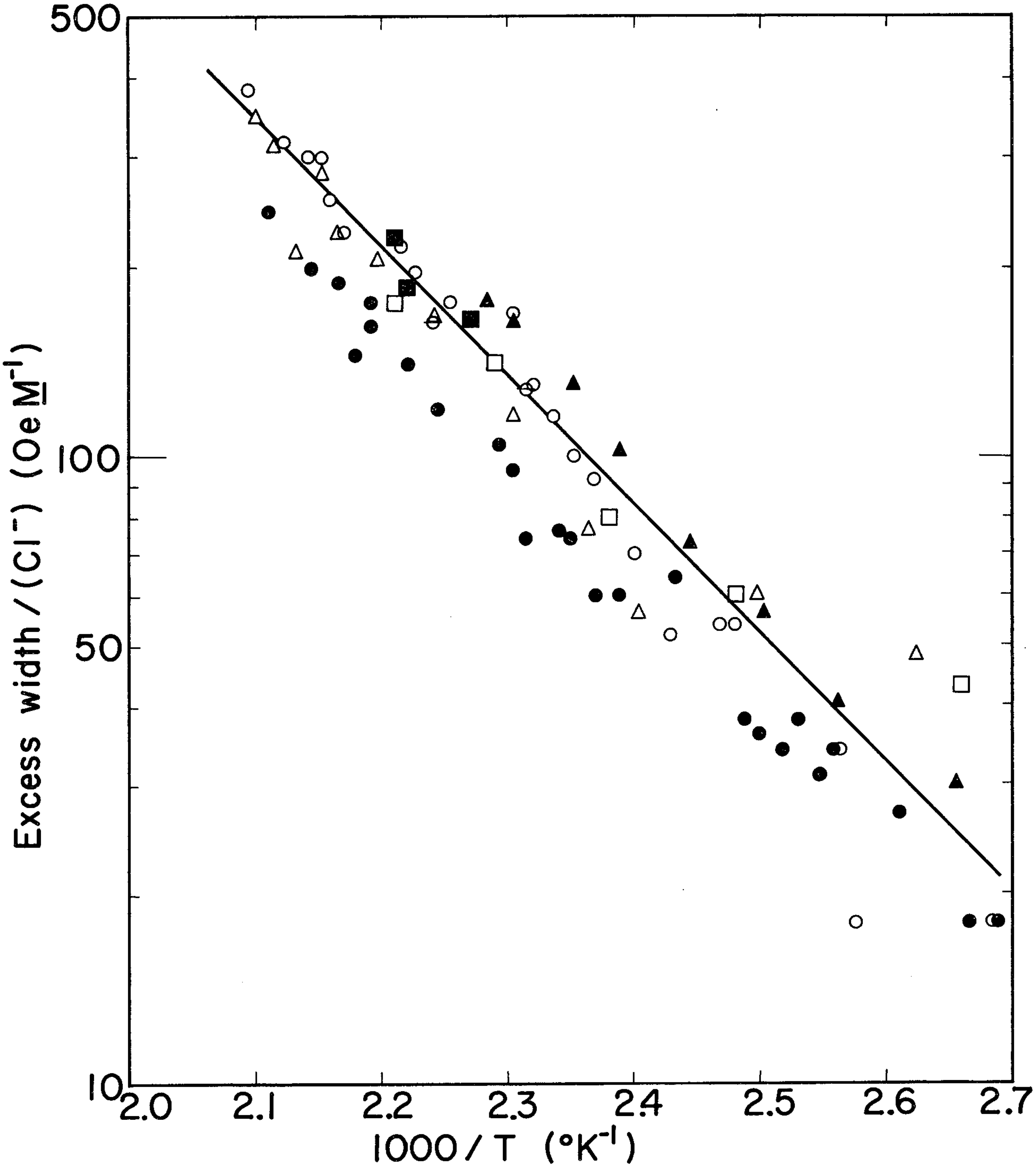
Figure 3. The effect of added Na_2SO_4 to 0.05$\underline{M}$ $Mn(ClO_4)_2$ in the amount: ⊖ 0.02$\underline{M}$, ⊙ 0.03$\underline{M}$, □ 0.04$\underline{M}$, ◉ 0.05$\underline{M}$, △ 0.1$\underline{M}$. The dashed curve is 0.05$\underline{M}$ $Mn(ClO_4)_2$ without added salt.

Figure 4. The direct effect of added Na_2SO_4 to 0.05$\underline{M}$ $Mn(ClO_4)_2$. In the range 20 - 80°C there is no consistent variation with temperature and the total spread of the data are shown.



30
25
20
15
10
Width (Oe)
20
40
60
80
100
120
140
160
180
200
T (°C)
0.1 M Cl⁻
0.1 M Cl⁻
0.05 M Cl⁻
0.025 M Cl⁻
0.1 M ClO4⁻
MU-28085

Fig. 1



MUB-1335

Fig. 2

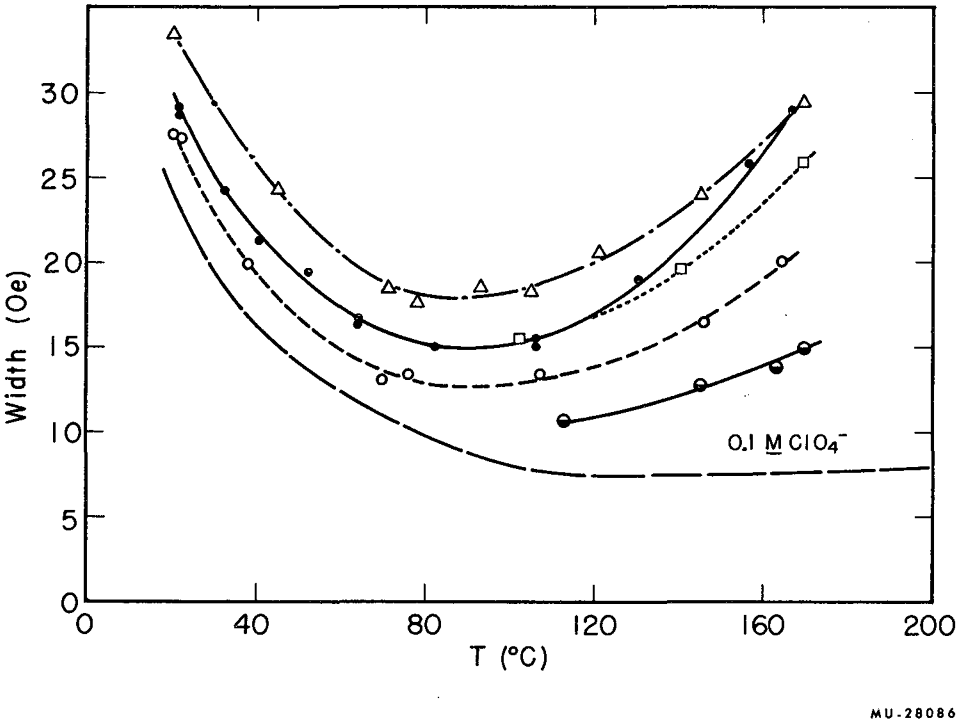
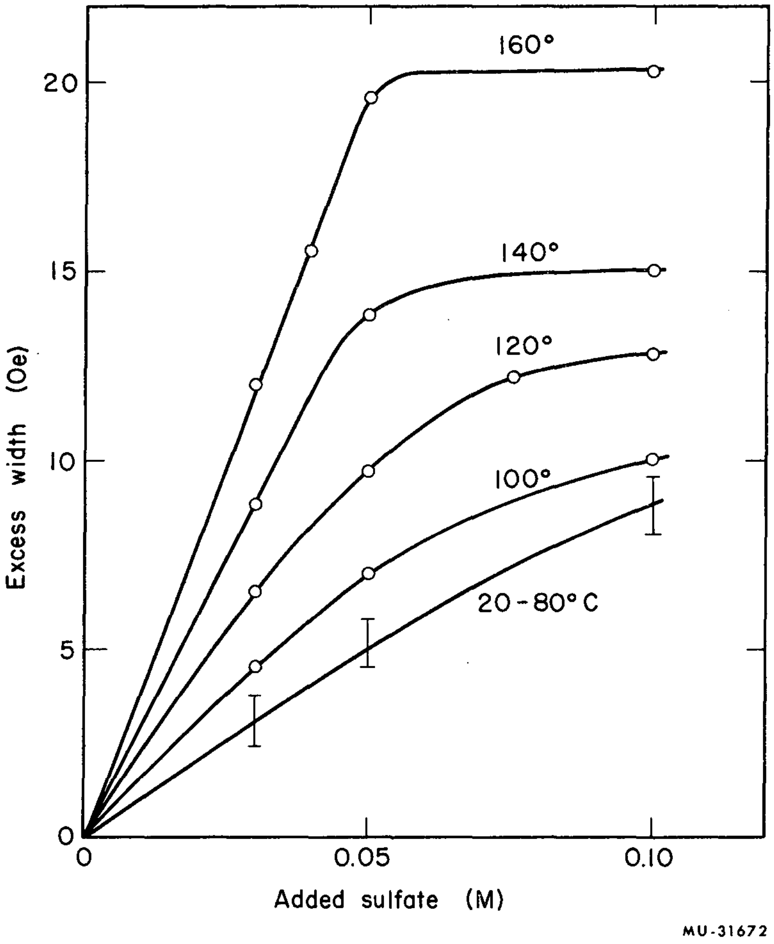


Fig. 3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140°
120°
100°
20-80°C
Excess width (Oe)
0
5
10
15
20
0
0.05
0.10
Added sulfate (M)
MU-31672

Fig. 4