Nuclear Magnetic Resonance Studies on the Existence of Perchlorate Complexes of Transition Metal Ions in Aqueous Perchloric Acid

BY FRANK KLANBERG, JOHN P. HUNT,[1] AND HAROLD W. DODGEN

The effects of the ions Mn^{++}, Fe^{3+}, Co^{++}, Ni^{++}, Cu^{++}, Ce^{3+}, and Be^{++} on the Cl^{35} n.m.r. absorption in ClO_4^- ion were studied in perchloric acid solutions. Only Mn^{++} of the above ions caused any detectable broadening of the resonance line. This broadening was studied as a function of concentration and temperature. The data lead to the conclusion that Mn^{++} forms a weak inner-sphere complex in perchloric acid. The absence of line broadening due to the other ions does not rule out possible complex formation with perchlorate ion. The broadening caused by Mn^{++} is attributed to an isotropic hyperfine spin interaction. Mn^{++}, Cu^{++}, Ni^{++}, and Fe^{3+} ions also were studied in saturated $NaClO_4$ solutions. Only Mn^{++} of the above ions caused any detectable broadening, and this was too small to be measured accurately. Mn^{++} in saturated $LiClO_4$ solution produced no detectable broadening. The small broadening in the perchlorate salt solutions relative to that in $HClO_4$ is ascribed to lower activity coefficients of the ClO_4^- in the salt solutions.

Introduction

The question of the existence of metal ion–perchlorate ion complexes is one of considerable interest and importance in aqueous solution chemistry because of the widespread use of perchlorate media for reference purposes, *e.g.*, in the determination of stability and rate constants. Such complexes, for example, have been reported to be formed in aqueous solution with ZrO^{++},[2] Fe^{3+},[3] and Ce^{3+} [4] ions. The precise nature of these complexes is still somewhat uncertain. The perchlorate ion may be present in the first or inner coördination sphere of the metal ion (inner-sphere complex) or it may be held outside this sphere, being separated from the metal ion by at least one water molecule (outer-sphere complex). It occurred to us that nuclear magnetic resonance spectroscopy might shed further light on the problem. There would seem to be at least two approaches to such a study.

First, it is plausible that the O^{17} resonance in perchlorate ion would be the most sensitive indicator of any interaction with the metal ions. Sufficiently enriched material for such an investigation was not available to us at the time of this study. Second, if the interaction is relatively strong, as might be expected for inner-sphere complexes, the position and/or line width of the Cl^{35} resonance could be affected. We have taken the latter approach and have examined the effects of various paramagnetic ions and of Be^{++} ions on the Cl^{35} resonance in perchlorate solutions.

Experimental

The nuclear magnetic resonance apparatus used was of conventional design employing a marginal oscillator, phase-sensitive detector, and a variable field electromagnet at *ca.* 9200 gauss. Derivatives of absorption curves were displayed on a recorder. The modulation amplitude and frequency and the radiofrequency power level could be varied as desired. The Cl^{35} resonance was observed at a constant frequency of *ca.* 3.861 Mc./sec. by sweeping the magnetic field. The observed line widths (W) were measured from the peak to peak distances of the derivative curve displayed on the recorder. Calibration of the sweep was effected using the known separations of the N^{14} lines in ammonium nitrate. The radiofrequency power levels were kept low enough to avoid saturation of the resonances. The observed line widths for sharp lines usually were larger than the natural widths due to the desirability of obtaining good signal-to-noise ratios, which required compromising in choice of modulation amplitude and frequency. Most of the work was done at a modulation frequency of 30 c./sec. and modulation amplitudes from 0.05 to 0.20 gauss. It was demonstrated that line broadenings (Δ), calculated by subtracting the observed line width for the perchloric acid solution from the observed line widths for metal ion solutions in perchloric acid measured under identical conditions, were not affected by choice of modulation parameters in the range used. The experimental error was *ca.* $\pm 10\%$ in the broadening. The usual procedure was to make four line width determinations on each sample, alternating the direction of field sweep. The reproducibility of the line widths was usually ± 0.03 gauss or better, broad lines having larger uncertainties.

The samples were contained in small stoppered Pyrex test tubes. Sample temperatures were controlled by an air thermostat device and measured by immersion of a small, glass-protected thermocouple in the solution.

Solutions were prepared using distilled water, C.P. perchloric acid, and the various salts (usually perchlorates), prepared and analyzed by standard procedures.

Results

A chemical shift of 970 p.p.m., relative to concentrated hydrochloric acid, for the Cl^{35} nucleus in perchloric acid solutions was observed. None of the added metal ions produced any detectable (>20 p.p.m.) additional shifts.

The observed line widths for Cl^{35} in perchloric acid solutions varied from 0.18 ± 0.03 gauss at 0.01 gauss modulation amplitude to 0.36 ± 0.03 gauss at 0.20 gauss modulation amplitude. At a given modulation amplitude the observed width was independent of acid concentration and temperature in the ranges used.

Results for the metal ion–perchloric acid solutions are given in Tables I and II and Fig. 1. Only Mn^{++} ion solutions of those studied showed any measurable

(1) To whom inquiries may be addressed.
(2) P. R. Murthy and C. C. Patel, *Naturwiss.*, **48**, 693 (1961).
(3) F. Sutton, *Nature*, **169**, 71 (1952).
(4) L. H. Sutcliffe and J. R. Weber, *Trans. Faraday Soc.*, **52**, 1225 (1956).

TABLE I

LINE BROADENING DATA FOR Mn^{++} SOLUTIONS IN PERCHLORIC ACID AT 27°

M HClO₄	M Mn(ClO₄)₂	$\Delta/(Mn)_0{}^a$ (gauss M^{-1})
5.0	0.91	0.33 ± 0.04
6.0	1.00	.39 ± .03
6.7	0.59	.54 ± .05
7.1	.60	.67 ± .05
7.5	.23	.56 ± .13
8.0	.10	1.0 ± .3
9.0	.080	1.1 ± .4
9.7	.080	2.6 ± .4
10.0	.060	2.7 ± .3
10.7	.045	4.7 ± .6
10.7	.089	4.8 ± .4
10.8	.10	5.6 ± .3
11.7	.050	10.8 ± 1.4
12.0	.050	14.2 ± 1.0
12.0	.050	14.6 ± 0.6
12.0	.10	15.4 ± 1.0

^{a} $(Mn)_0$ refers to total manganese concentration.

TABLE II

LINE WIDTHS FOR VARIOUS IONIC SOLUTIONS IN PERCHLORIC ACID AT 26°

Ion	M Ion	M HClO₄	W obsd. (gauss)	W HClO₄ (gauss)	Salt anion
Ce³⁺	0.10	12.0	0.15 ± 0.03	0.19 ± 0.02	NO₃⁻
Fe³⁺	0.10	6.0	.38 ± .02	.36 ± .02	ClO₄⁻
Fe³⁺	4.5	4.8	.39 ± .01	.36 ± .02	ClO₄⁻
Fe³⁺	Saturated	12.0	.43 ± .03	.41 ± .02	ClO₄⁻
Ni⁺⁺	0.10	8.0	.38 ± .01	.36 ± .01	ClO₄⁻
Ni⁺⁺	4.75	3.0	.35 ± .01	.36 ± .02	ClO₄⁻
Ni⁺⁺	Saturated	12.0	.21 ± .03	.23 ± .03	NO₃⁻
Cu⁺⁺	0.10	12.0	.39 ± .04	.36 ± .02	ClO₄⁻
Cu⁺⁺	3.5	6.0	.38 ± .02	.36 ± .02	ClO₄⁻
Co⁺⁺	0.075	9.0	.38 ± .04	.36 ± .02	ClO₄⁻
Co⁺⁺	2.6	3.9	.38 ± .03	.36 ± .03	ClO₄⁻
Co⁺⁺	Saturated	12.0	.22 ± .03	.23 ± .03	SO₄²⁻
Be⁺⁺	Saturated	12.0	.22 ± .03	.22 ± .03	ClO₄⁻

line broadenings. The salt concentrations that could be used were severely limited by their solubility properties. The line broadenings produced by Mn^{++} ion were appreciably increased as the temperature was lowered (Fig. 1).

In addition, saturated solutions of manganous and ferric perchlorates and cupric and nickelous nitrates in saturated sodium perchlorate solution (ca. 8.6 M at room temperature) were investigated. Mn^{++} gave a
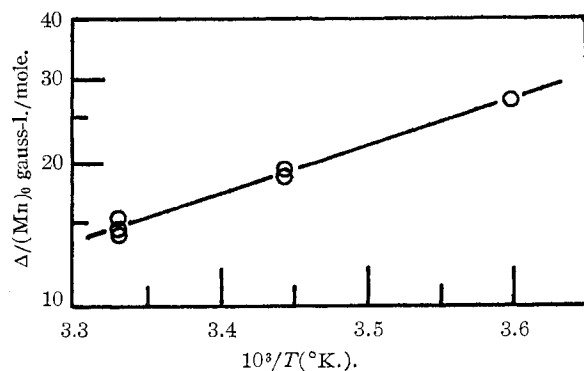

Fig. 1.—Temperature dependence of $\Delta/(Mn)_0$.

barely detectable broadening in the saturated solution (ca. 0.50 M in Mn), while the other solutions showed no effects due to the presence of the metal ions. Manganous perchlorate at ca. 0.4 M in 6.7 m lithium perchlorate showed no detectable broadening.

Some experiments were performed to test for oxidation–reduction in our system. Traces of ClO_3^-, ClO_2^-, ClO_2, and Cl_2 were shown to be absent using I^- which previously had been shown to yield I_2 when the above chlorine species were deliberately added. No evidence for Cl^- could be obtained using Ag^+. Likewise no evidence for higher oxidation states of Mn was found.

The addition of ClO_3^- to concentrated HClO₄ produced no change in the line width of the ClO_4^-. ClO_2 and ClO_4^- form quite rapidly from ClO_3^- in such solutions. Addition of ClO_3^- to give 0.01 M ClO_3^- in a solution 0.05 M in Mn^{++} and 12 M in HClO₄ did not immediately change the line width from that found in the absence of the ClO_3^-. In a few minutes, MnO_2 precipitated and the ClO_4^- line became sharp, as expected because of the removal of the manganese from solution.

Discussion

The observed broadenings of the Cl^{35} line in ClO_4^- require some mechanism involving a rapid exchange of the Cl^{35} between different sites. One possibility might be rapid exchange involving another oxidation state of chlorine. We believe our results concerning the effects of added ClO_3^- rule out this possibility. In our opinion the only plausible remaining explanation involves formation of a weak inner-sphere Mn^{++}–ClO_4^- complex. In the following discussion we proceed to show that the detailed results are consistent with the postulated formation of such a complex.

Using the usual treatment[5] of a two-site problem in the limit of "rapid exchange" we have

$$1/T_2 = p_A/T_{2A} + p_B/T_{2B} \qquad (1)$$

where T_2 is the observed transverse relaxation time of the Cl^{35} in the presence of metal ion, T_{2A} is the transverse relaxation time of Cl^{35} in perchloric acid alone, T_{2B} the same in the presumed complex, p_A is the mole fraction of free perchlorate ion, and p_B is the mole fraction of perchlorate ion in the complex. Assuming the equilibrium

$$Mn^{++} + ClO_4^- \rightleftharpoons MnClO_4^+ \text{ with } K_1 =$$
$$(MnClO_4^+)f_+/(Mn^{++})(ClO_4^-)f_{++}f_- \qquad (2)$$
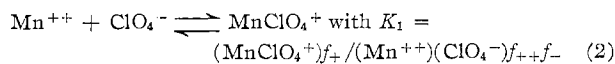
where the parentheses represent molar concentration and f the relevant activity coefficients, and assuming further that $(MnClO_4^+) \ll (Mn)_0$ or (ClO_4^-), one can calculate p_A and p_B and substitute the results into (1). The result is

$$1/T_2 - 1/T_{2A} = (1/T_{2B} - 1/T_{2A})K_1(Mn)_0f_{++}f_-/f_+ \qquad (3)$$

(5) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 218.

where $(Mn)_0$ represents the total manganese concentration. Finally, eq. 3 may be written

$$\Delta/(Mn)_0 = (2/\sqrt{3}\gamma)(1/T_{2B} - 1/T_{2A})K_1 f_{++} f_- /f_+ \quad (4)$$

where $\Delta = (1/T_2 - 1/T_{2A})(2/\sqrt{3}\gamma)$ and the relation $\gamma W \sqrt{3}/2 = 1/T_2$ for Lorentzian line shapes has been used. γ is the magnetogyric ratio for Cl^{35} and W the line width between points of inflection of the absorption curve.

If one considers the case of "slow exchange," makes the above assumptions concerning equilibrium (eq. 2), and further assumes that the rate of formation of $MnClO_4^+$ is first order in (Mn^{++}) and first order in (ClO_4^-), one obtains the result

$$\Delta/(Mn)_0 = (2/\sqrt{3}\gamma)kf_{++} f_- /f_+ * \quad (5)$$

where k is the specific rate constant for formation of $MnClO_4^+$, f_+* is the activity coefficient of the activated complex, and the other symbols have the same meaning as in eq. 4.

Inspection of the right hand side of eq. 4 and 5 shows that both predict a smooth variation of $\Delta/(Mn)_0$ with perchloric acid concentration. A semi-log plot of $\Delta/(Mn)_0$ vs. $(HClO_4)$ is shown in Fig. 2 and similar plots of the mean molar ion activity coefficient $(f_\pm)$ of perchloric acid and the coefficient of viscosity (η) of perchloric acid vs. $(HClO_4)$ are given in Fig. 3. The similarity of Fig. 2 and the activity coefficient plot of Fig. 3 is striking and strongly suggests that f_- dominates in determining the shape of the curve in Fig. 2. It is at least qualitatively reasonable that f_- would follow $f_\pm$ of perchloric acid and that the other f values $(f_{++}/f_+$ or $f_{++}/f_+*)$ would not vary as drastically. There appears to be no way of evaluating K_1 in view of the many unknown quantities involved.

Since, in eq. 4, $1/T_{2B} \gg 1/T_{2A}$ (condition for observable broadening) and the value of $1/T_{2B}$ might depend on a tumbling or diffusion correlation time, the change in viscosity of the solution also may be contributing to the shape of the curve in Fig. 2.

As seen from the above discussion, a choice between the rapid and slow exchange cases cannot be made on the basis of the concentration dependence data. In either case, however, the data can be understood in terms of complex formation. The observed temperature dependence of the line broadening might suggest that the rapid exchange case is at hand since slow exchange usually exhibits the chemical, Arrhenius type of behavior. A more detailed analysis, however, indicates that in the present case, at least, the temperature dependence may not serve to distinguish rapid and slow exchange. One obtains for the rapid exchange case the result

$$[\partial \ln (\Delta/(Mn)_0)/\partial T]_{P,N} = \partial \ln (1/T_{2B} - 1/T_{2A})/\partial T +$$
$$\Delta H^0/RT^2 - (\bar{L}_{++} + \bar{L}_- - \bar{L}_+)/RT^2 \quad (6)$$

where ΔH^0 is the standard enthalpy of formation of the complex and the $\bar{L}$'s are the relevant relative partial molar heat contents of the ions involved. For the slow exchange case, using the absolute reaction rate theory, one obtains
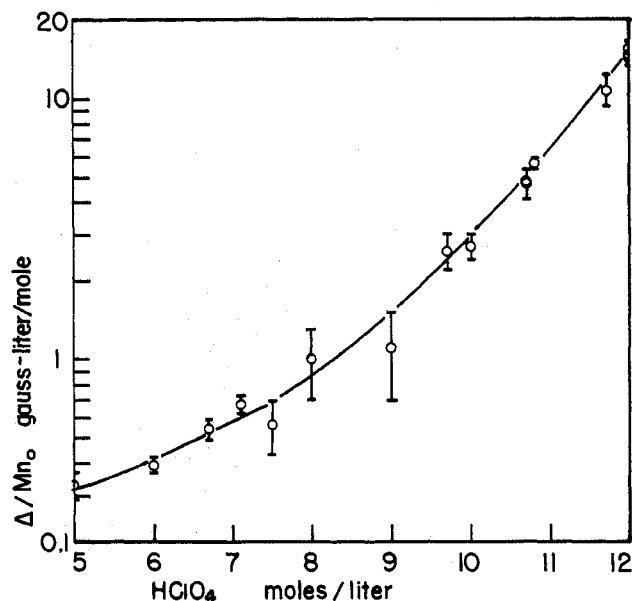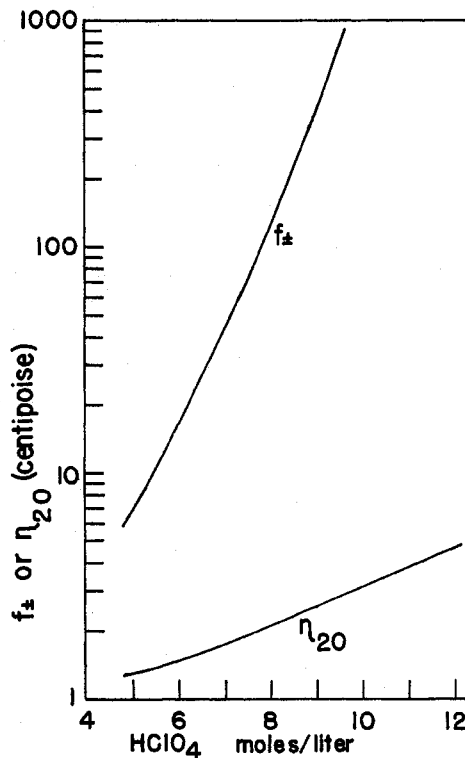

Fig. 2.—$\Delta/(Mn)_0$ *vs.* $(HClO_4)$.

Fig. 3.—$f_\pm$ and η_{20} of $HClO_4$ *vs.* $(HClO_4)$.

$$[\partial \ln (\Delta/(Mn)_0)/\partial T]_{P,N} = 1/T +$$
$$\Delta H^{0*}/RT^2 - (\bar{L}_{++} + \bar{L}_- - \bar{L}^*_+)/RT^2 \quad (7)$$

where ΔH^{0*} is the standard enthalpy of activation and the $\bar{L}$'s again are relative partial molar heat contents. In dilute solutions the $\bar{L}$'s usually are assumed to be small and are ignored. In 12 M perchloric acid it seems likely that $\bar{L}_-$ at least might be quite large since the heat of dilution of perchloric acid is considerable. An estimate of $\bar{L}_\pm$ for 12 M perchloric acid was made from the data of Berthelot[6] and is $+11$ kcal./mole. The apparent enthalpy change calculated from the slope in

(6) M. Berthelot, *Ann. chim. phys.*, [5] **27**, 223 (1882).

Fig. 1 is -4.5 kcal./mole. Unfortunately, there seem to be no data that would give even approximate values for the $\bar{L}$'s of the positive ions in this medium so that the total contribution to the apparent enthalpy cannot be assessed. Experimentally, we have been unable to measure the temperature dependence of the line broadening at low perchloric acid concentrations, where the $\bar{L}$'s would be expected to be small. It would be necessary to be able to measure much smaller line broadenings than our equipment permits so as to use low manganese concentrations and thus avoid the problems due to change in solubility with temperature. It seems quite possible that in this case the various terms contributing to the temperature coefficient are similar in magnitude and that the over-all effect cannot be simply interpreted.

The argument for an inner-sphere complex requires consideration of the possible origins of the observed broadening. Nuclear electrical quadrupole broadening and the magnetic isotropic hyperfine interaction appear to be the most likely sources. The absence of broadening effects for all ions but Mn^{++} suggests that the quadrupole effects are small. Be^{++} ion was tried because it was thought that quadrupole effects might appear. A rough calculation of the expected quadrupole effect suggests also that the effect would be too small to explain the observed broadenings. It seems significant that Mn^{++} has the longest electron spin relaxation time of all the ions studied (*ca.* 3×10^{-9} sec.).[7,8] It also is well known that Mn^{++} is particularly effective in relaxing nuclear spins. Effects on protons in the case of the hydrated Mn^{++} ion have been explained on the basis of the interaction of electron and nuclear spins,[9] and it seems likely that the perchlorate case is similar. The

(7) N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, **34**, 842 (1961).
(8) A. Abragam, "The Principles of Nuclear Magnetism," Oxford Univ. Press, London, 1961, p. 330.
(9) See for example, L. O. Morgan and A. W. Nolle, *J. Chem. Phys.*, **31**, 365 (1959).

absence of broadening in the cases of the other ions studied then may be due to the short electron spin relaxation times involved, and complexes cannot be ruled out on the basis of the data obtained here. Since the Mn^{++} ion is separated from the Cl^{35} by at least one oxygen atom it appears that some covalent bonding is involved between the Mn^{++} and ClO_4^- ions. An outer-sphere complex presumably would involve largely ionic hydrogen bonding between the hydrated cation and the perchlorate ion, and, in addition, at least two oxygen atoms and a hydrogen atom would be interposed between the two relevant centers. It seems to us very unlikely that this situation would give rise to any significant broadening of the Cl^{35} absorption line. Therefore, we consider the formation of an inner-sphere complex to be the most probable explanation of our findings. A single experiment using 12 M $HClO_4$ saturated with Gd^{3+} (*ca.* 0.05 M) showed no broadening detectable with our apparatus. Gd^{3+} has a relatively long electron spin relaxation time but the f electrons are not likely to be involved in the binding even if a ClO_4^- complex exists and thus broadening would not be observed.

The observation of a Mn^{++}–perchlorate complex in perchloric acid appears to be due to a combination of the great effectiveness of Mn^{++} ion in relaxing nuclear spins and the high activity coefficients of perchloric acid. The high activity coefficients probably are related to the relatively small amount of "free water" in the solutions, since the hydrated protons may tie up a considerable amount of water. In the most concentrated solutions there may not be enough water to satisfy both the protons and the manganous ions, and it is conceivable that at least one perchlorate ion might be found in the first coördination sphere of Mn^{++}. The broadening effect persists, however, even in 5 M acid where considerably more water is available for hydrating the ions. We feel, therefore, that our results have practical chemical significance for the study of equilibrium and rates in solutions containing perchlorate ions.

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Some New Asymmetric Octahedral Complexes of Arsenic(V)

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The complexes formed with arsenic acid and the four ligands 4-chlorocatechol, 3-methylcatechol, 4-methylcatechol, and 2,3-dihydroxynaphthalene have been prepared, characterized, and resolved. All of these complexes undergo a second-order asymmetric transformation in alcoholic solution in the presence of suitable alkaloids.

The present study was concerned with the preparation, characterization, and resolution of complexes of arsenic acid with *o*-dihydroxy aromatic compounds. Earlier studies of the organic complexes of arsenic(V)

have been concerned almost exclusively with the catechol complex. This was prepared by Weinland and Heinzler,[2] resolved by Rosenheim and Plato,[3] and sub-

(1) To whom correspondence concerning this paper should be addressed.

(2) R. Weinland and J. Heinzler, *Ber.*, **52**, 1316 (1919); **53**, 2765 (1920).
(3) A. Rosenheim and W. Plato, *ibid.*, **58B**, 2000 (1925).