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Oxygen-17 Nuclear Magnetic Resonance Studies of Aqueous Nickel Ion

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Abstract

In aqueous solutions of nickelous ion the bulk water NMR linewidths of oxygen-17 have been measured from about 0° to 150°C at 2.00 MHz and 8.134 MHz. The chemical shift of bulk water oxygen was similarly measured at 8.134 MHz. The ^{17}O NMR spectrum of water in the first coordination sphere of Ni^{2+} ion has been reexamined under more favorable experimental conditions. The results of these studies are consistent with six equivalent waters composing the first coordination sphere of Ni^{2+} over the temperature range covered. The enthalpy and entropy of activation for water exchange has been calculated to be 13.9 kcal/mole and 10 eu respectively with a scalar coupling constant (A/h) to the ^{17}O of $2.4 \times 10^{+7}$ Hz.

In agreement with the results of Fiat a small residual chemical shift of ^{17}O of bulk water was observed at low temperature. It is concluded that the shift must be attributed to second coordination sphere interactions.

The experimental frequency dependence of the relaxation of ^{17}O caused by scalar coupling has been used to calculate a correlation time for the electronic relaxation of Ni^{2+} of 1.1×10^{-12} sec at 160°C. In the low frequency limit at 2.00 MHz, the electronic relaxation times, T_{1e} and T_{2e}, are found to be 5.8×10^{-12} sec at 160°C with an activation energy of 1.2 kcal/mole.

Another independent measure of the electronic relaxation correlation time has been obtained by extending the work of Morgan and Nolle on protons to 220 MHz. The apparent lack of a dispersion region in the frequency dependence of the dipolar coupling to the protons has been shown to be due to a competing frequency dependence of the electronic relaxation. An electronic correlation time of 1.0×10^{-12} is consistent with these data as well.

Introduction

The first hydration sphere of nickelous ion in aqueous solution has been studied in the past by ^{17}O NMR.[1-4] The results of these studies have led to some perplexing contradictions which have cast doubt on the previous chemical knowledge of the Ni^{2+} ion or on the adequacy of the general exchange theory governing NMR linewidths. From proton nuclear magnetic resonance measurements near -30°C in concentrated aqueous salt solutions, Swift and Weinberger[5] found a coordination number of six for nickel ion. Fiat[3] has interpreted the oxygen-17 data at temperatures above 0°C as evidence for four "slowly" exchanging waters and two more rapidly exchanging waters. While the two sets of data are not necessarily in conflict because of the temperature differences, such an implied inequivalence of the six first coordination sphere waters is unexpected on the basis of other chemical properties.

A recalculation of the relaxation processes for oxygen-17 in solutions of nickelous ion which made use of estimates of the electronic relaxation time[2,6] of Ni^{2+}, has revealed that there is an appreciable contribution from the scalar coupling relaxation process in addition to the $\Delta\omega$ process at temperatures above 70°C. More importantly, the earlier data at 2MHz[1] were found to be inconsistent with theory, if the electronic relaxation time estimates are correct.

Also Morgan and Nolle[6] were unable to find the frequency dependence expected from theory of the longitudinal and transverse relaxation times of protons of water in solutions of nickelous ion. They could find no frequency dependence whatsoever up to 60 MHz.

The purpose of the present work is to clear up these apparent contradictions.

Theory

A discussion of the transverse relaxation of the bulk waters due to exchange with dilute paramagnetic metal ions has been given by Swift and Connick.[1] They found the contribution to the bulk water relaxation time, T_{2p}, arising from the presence of dilute paramagnetic metal ions could be described by the following formula

$$\frac{1}{T_{2p}} = \frac{P_m}{\tau_m} \frac{\frac{1}{T_{2m}^2} + \frac{1}{T_{2m}\tau_m} + \Delta\omega_m^2}{\left[\left(\frac{1}{T_{2m}} + \frac{1}{\tau_m}\right)^2 + \Delta\omega_m^2\right]} \qquad (1)$$

where τ_m is the lifetime of the water molecules in the first coordination sphere of the paramagnetic metal ion, $\frac{1}{T_{2m}}$ is the rate of the relaxation of the ^{17}O of the bound waters, $\Delta\omega_m$ is the difference in resonance frequency of the bound waters and the observed resonance, and P_m is a mole ratio of the waters in the bound sites to those elsewhere. P_m is given by:

$$P_m = \frac{x_m}{x_{H_2O}} = \frac{n[Ni^{2+}]}{55.5 - n[Ni^{2+}]} \qquad (2)$$

where x is the mole fraction of oxygen nuclei of water in the indicated environment, n is the coordination number of the paramagnetic ion and brackets indicate the concentration of the enclosed species in moles per 1000 grams of water. No simplification of equation (1) is adequate in describing the entire temperature range covered for Ni^{2+}.

The bulk water chemical shift has been shown by Swift and Connick[1] to obey equation (3).

$$\Delta\omega_{H_2O} = \frac{-P_m \Delta\omega_m}{\tau_m^2 \left[\left(\frac{1}{T_{2m}} + \frac{1}{\tau_m} \right)^2 + \Delta\omega_m^2 \right]} \tag{3}$$

The notation is identical to equation (1). The chemical shift of the bound waters relative to pure water, $\Delta\omega_{H_2O\text{-}m}$, is expected to be given by the Bloombergen equation[7]

$$\Delta\omega_{H_2O\text{-}m} = \omega\, S(S+1)\, \frac{g_{eff}\,\beta}{\gamma_I}\, \frac{A}{3kT} \tag{4}$$

where ω is the precessional frequency of the nuclei in question, $g_{eff}\,\beta$ and γ_I are the gyromagnetic ratios of the unpaired electrons and the nucleus, A is the scalar coupling constant in ergs and S is the electron spin quantum number.

The temperature dependence of the exchange lifetime is expected to follow the familiar expression for the rate of chemical reaction

$$\tau_m = \frac{h}{kT} \exp\left[\frac{\Delta H^{\ddagger}}{RT} - \frac{\Delta S^{\ddagger}}{R} \right] \tag{5}$$

where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the enthalpy and entropy of activation for water exchange.

The relaxation of ^{17}O caused by the Ni^{2+} ion has been shown to be due to scalar coupling[1,2] which has the following functional form:[8]

$$\frac{1}{T_{2m}} = \frac{S(S+1)}{3} \left(\frac{A}{\hbar} \right)^2 \tau_e \tag{6}$$

$$\tau_e = \left[T_{1e} + \frac{T_{2e}}{1 + \omega_S^2 T_{2e}^2}\right] \qquad (7)$$

where T_{1e} and T_{2e} are the longitudinal and transverse relaxation times of the electrons and ω_S is the precessional frequency of the electrons. The coupling mechanism between the Ni^{2+} ion and the water protons can easily be shown to be dominated by a dipole-dipole interaction. The scalar coupling constant in this case is known to be 1.1×10^5 cps.[9] Using the electronic relaxation times in Table I in equation (6) for a 0.1 M solution yields a value $T_2\,[Ni^{2+}] = 5.75$. Comparison of this value with the data in Fig. (5) shows the scalar contribution to the total linewidth to be negligibly small. The dipolar coupling expression for the present conditions is[2,10,11]

$$\frac{1}{T_2} = \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \frac{1}{15d^6} \left\{7\, T_{1e} + \frac{13T_{2e}}{1 + \omega_S^2 T_{2e}^2}\right\} \qquad (8)$$

where γ_I and γ_S are the gyromagnetic ratios of the nucleus and the electrons, d is the distance of separation of the two dipoles, ω_S is the precessional frequency of the electrons, and T_{1e} and T_{2e} are the transverse and longitudinal relaxation times of the paramagnetic electrons on Ni^{2+}.

Experimental

Dilute nickelous perchlorate solutions in 10 percent $H_2{}^{17}O$ were prepared in the following manner. A stock solution of $Ni(ClO_4)_2 \cdot 6H_2O$

was prepared from reagent grade crystals in natural abundance distilled water. The solution was analyzed to be 1.249 M[12] in Ni^{2+} with no detectible amounts of other paramagnetic impurities. Solutions of ca. 1 ml. volume and desired concentration were then prepared by analytic dilution of the stock solution. Perchloric acid was added in all cases to a concentration of 0.10 M. The water was then distilled off in vacuum and water enriched to 10 percent $H_2{}^{17}O$ distilled into the sample. Weight differences indicated the amount of natural abundance water removed and enriched water added. The concentration of the final sample could be easily calculated. The sample for the bound water studies was prepared in ca. 20 percent $H_2{}^{17}O$ enriched water normalized in deuterium obtained from the Weizman Institute. To avoid isotopic dilution reagent grade anhydrous silver perchlorate and anhydrous nickelous chloride were mixed in the appropriate molar amounts in the 20% enriched water. The silver chloride precipitate was separated from the solution by decantation. The solution was analyzed to be 3.70 M in Ni^{2+}.

The bulk water ^{17}O resonance signals were recorded with a Varian Associates Model V-4200 wide-line spectrometer operated at 8.134 and 2.000 MHz. Temperature was controlled by flowing heated or cooled dry nitrogen past the sample. The probe was protected from damaging temperatures by a dewared insert into which the sample was placed. The temperature was measured to ± 0.1°C with a copper-constantin thermocouple immediately outside the sample tube and regulated to ± 0.5°C.

Chemical shifts were measured by successive scans of the sample and a standard pure water sample replaced between scans. The large magnetic field was varied by passing a ramp D. C. current through the modulation coils of the probe. Linear extrapolations between the position of resonance of the standard as a function of time allowed for a correction of the errors due to drift in the large magnetic field.

Bound water measurements were recorded on the same instrument at a fixed frequency of 8.134 MHz. Signal averaging was accomplished using a Varian Associates Model 1024 time averaging computer. The internal ramp of the computer was fed directly to the sweep input of the power supply with the super stabilizer removed from the system. Derivative mode detection was employed with care being taken to avoid modulational broadening. A measurement of absolute field as a function of magnet current was made using a spinning coil gaussmeter for the determination of the chemical shifts.

Results and Discussion

Bulk Water Measurements

The bulk water relaxation data are given as a function of the reciprocal of the absolute temperature at 8.134 MHz in Fig. (1) and 2.00 MHz in Fig. (2). The data are tabulated in Tables I and II. The solid curve through the data points in Fig. (1) is a theoretical calculation using equation (1) and the parameters given in Table III which were determined from a computer fit to all of the data

Table III.

Parameters Determined by Fitting Relaxation Data

	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (eu)	$\frac{A}{h}$ (Hz)	$\tau_e°$ (sec)	V(kcal)
8.134 MHz	13.9	10	2.4×10^{7}	3.8×10^{-12}	0.6
2.000 MHz				2.36×10^{-12}	1.2

Table I.

Bulk Water Relaxation Data at 8.13 MHz

$10^3/T$ °K^{-1}	$T_{2_{H_2O}}$ msec	T_{2p} msec	$P_m x10^3$
3.357	6.60	13.4	2.357
3.309	7.20	9.62	2.357
3.196	8.85	4.53	2.357
3.085	11.4	2.28	2.357
3.008	13.2	1.52	2.357
2.946	14.5	1.27	2.357
2.878	16.1	1.40	2.357
2.704	20.5	1.93	2.357
2.587	23.6	2.28	2.357
2.514	26.3	2.37	2.357
2.444	29.6	2.63	2.357
3.357	6.60	12.27	2.357
3.305	7.25	9.29	2.357
2.997	13.3	1.43	2.357
2.921	15.1	1.24	2.357
2.860	16.5	1.22	2.357
2.820	17.4	1.37	2.357
2.486	27.6	2.63	2.357
2.412	31.0	2.60	2.357
2.342	34.9	2.75	2.357
3.358	6.36	8.21	3.395
3.212	8.60	3.17	3.395
3.121	10.5	1.95	3.395

Table I. (continued)

$10^3/T$ °K^{-1}	$T_{2_{H_2O}}$ msec	T_{2p} msec	P_m x10^3
3.010	13.1	1.08	3.395
2.814	17.7	1.00	3.395
2.925	15.1	0.917	3.395
3.621	3.3	37.58	3.395
3.531	4.4	23.25	3.395
3.469	5.25	18.47	3.395

Table II.

Bulk Water Relaxation Data at 2.00 MHz

$10^3/T$ °K^{-1}	$T_{2_{H_2O}}$ msec	T_{2p} msec	$P_m x10^3$
2.363	31.0	1.66	3.395
2.389	30.1	1.71	3.395
2.441	28.3	1.70	3.395
2.480	27.1	1.89	3.395
2.564	24.5	1.84	3.395
2.687	21.0	2.03	3.395
2.754	19.0	2.16	3.395
2.822	17.5	3.08	2.357
2.825	17.5	2.22	3.395
2.941	14.7	3.43	2.357
2.949	14.6	2.39	3.395
3.021	12.8	2.51	3.395
3.107	10.8	3.04	3.395
3.111	10.7	4.38	2.357
3.241	8.08	5.14	3.395
3.244	8.05	6.85	2.357
3.367	6.28	10.33	3.395
3.382	6.26	15.91	2.357
3.383	6.25	9.41	3.395

using a convergent nonlinear least squares curve fitting technique. In these calculations, and those which follow, the results are dependent upon the g value for the electron. This value has never been measured for Ni^{2+} in aqueous solution. ESR work on hydrated salts of Ni^{2+} indicates an isotropic g value of 2.25 which is relatively independent of the anions involved.[13] The assumption will be made that this value is the same for solutions.

The $\tau_e°$ and V in Table III are defined by

$$\tau_e = \tau_e° \exp \frac{V}{RT} \qquad (9)$$

where τ_e is the effective electronic relaxation time for Ni^{2+} as defined in equation (7) and V is the activation energy for the electronic relaxation. V was not a parameter in the computer program. The fit to the 8.134 MHz data is insensitive to the value of V from 0 to 2 kcal. The value of 0.6 kcal was chosen for reasons to be discussed below. Since the 2.000 MHz data are relatively insensitive to $\frac{A}{h}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ over the temperature range covered, the 8.134 MHz parameters were used in the calculation of the theoretical curve in Fig. (2). Only the $\tau_e°$ and V had to be changed in order to fit the 2.00 MHz data. These values are given in Table I.

The values for $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\frac{A}{h}$ vary significantly from those given earlier.[1,2] The variations appear to be due to the previous neglect of the $\frac{1}{T_{2m}}$ term and to less accurate, noncomputer fits to the data.

In Figs. 1 and 2 the deviations from the straight lines observed at low temperatures may not be real. The vertical error lines correspond to one standard deviation, but the water blank is quite large. For example at the lowest point in Fig. 1, the value of $\frac{1}{T_{2p}}$ was only 1/10 of the observed linewidth. Calculations show that the deviations could not be from dipole-dipole, scalar, or quadrupole coupling effects in the second coordination sphere.

More recently A. G. Desai, H. W. Dogen and J. P. Hunt[4] have gathered data at 14.1 MHz from 0° to 88° C. In exchange controlled region their 14.1 MHz data are in complete agreement with our 8.13 MHz data. However their $\Delta H^{\ddagger}$ calculated from the 14.1 MHz data is only 12.3 kcal/mole. The agreement of the two sets of experimental points lends credence to the to the observation that the exchange controlled region could be best fit by a curved line with increasing slope at higher temperatures. The value of $\Delta H^{\ddagger}$ appears to change from about 11 kcal/mole near 0°C to nearly 14 kcal/mole at 60°C. This result could be formally described by an apparent $\Delta C_p^{\ddagger}$ equal to about 40 cal/deg. The $\Delta H^{\ddagger}$ reported for the 8.13 MHz data is an average value giving the best fit to our data from 0° to ca. 130°. No attempt was made to computer fit the data with a variable $\Delta H^{\ddagger}$ because of the smallness of the curvature.

The chemical shift of the bulk water can provide a check on the accuracy of the parameters in Table III. Figure 3 gives the experimental data as a function of the reciprocal of the absolute temperature. The solid line is the result of a calculation based on equation (3) and the parameters in Table III. The agreement is seen to be excellent in the high temperature region which is most sensitive to the parameters. The lower temperature shifts deviate systematically from the predicted contribution from the first coordination sphere. This effect has been observed previously[3] and was then attributed to two of the six bound water molecules which were hypothesized to exchange much faster than the other four. As will be shown below, direct observation of the chemical shift of the bound water resonance is inconsistent with this interpretation

Bound Water Measurements

A representative spectrum of the bound water resonance is shown in Fig. (4). The temperature was controlled through the use of a dewared insert between the sample and the probe. The use of water enriched to 20 percent $H_2{}^{17}O$ and employment of signal averaging gave a significant improvement in resolution over the previous work.[2]

The bound water chemical shift data are summarized in Table IV for several temperatures. The chemical shift has the expected $\frac{1}{T}$ dependence.

Table IV.

Bound Water Chemical Shift Measurements

	1.5°C	8.0°C	24.6°C	33°C
$\Delta\omega_{H_2O-m}$(Hz)	1.23×10^5	1.18×10^5	1.11×10^5	1.08×10^5

The bound water linewidth can be shown in the limit of large chemical shift to be

$$\frac{1}{T_2} = \frac{1}{T_{2m}} + \frac{1}{\tau_m} \qquad (10)$$

and should increase with increasing temperature because of the temperature dependence of $\frac{1}{\tau_m}$. This is verified experimentally. The experimental value for $\frac{1}{T_{2m}}$ is obtained by subtracting $\frac{1}{\tau_m}$ known from bulk water measurements from the measured bound water linewidth. These results are shown plotted as triangles in Fig. 1 and are seen to agree within experimental uncertainties with the calculated line labelled T_{2m}. The method of calculation of this line will be explained later.

Even with the improved experimental conditions an accurate coordination number from relative signal intensities could not be obtained. A more accurate method is available by combining the bulk and bound water chemical shift data.

In the limit of rapid exchange equation (3) reduces to

$$\Delta\omega_{H_2O} = - P_m \Delta\omega_m = - x_m \Delta\omega_{H_2O\text{-}m} \qquad (11)$$

where x_m is the mole fraction of oxygen nuclei of the water in the first coordination sphere of the nickel ions and $\Delta\omega_{H_2O\text{-}m}$ is the difference in resonance frequency of the oxygen of pure water and the oxygens of waters coordinated to nickel ion. (This equation is actually exact for rapid exchange regardless of the metal ion concentration). Substituting for x_m from equation (2) and rearranging

$$n = \frac{(55.5)\Delta\omega_{H_2O}}{[Ni^{2+}]\Delta\omega_{H_2O\text{-}m}} \qquad (12)$$

The line $\Delta\omega_m$ is shown in Fig. (3) and is approached above about 127°C. The bound water chemical shift can be calculated at this temperature using equation (4) and the value at low temperature. The value when inserted in equation (12) yields

$$n = 6.0 \pm 0.20$$

which agrees excellently with the measurement of Swift and Weinberger[5] from proton NMR at lower temperature. Thus it is concluded that, contrary to earlier evidence, the oxygen-17 NMR data are consistent with a six fold coordination of nickel ion with all six waters equivalent.

The above conclusion requires that the low temperature chemical shift discussed previously be attributed to waters outside the first coordination sphere. A similar effect of nearly equal magnitude has been observed[14] for Cr^{3+} which, because of the extremely slow first sphere exchange rate, can be due only to water outside the first coordination sphere.

The magnitudes and direction of the shifts can help to identify the type of orbitals of the metal ion involved in the interaction with second coordination sphere oxygens.[15] Donation of electron density by the oxygen into a half filled orbital of the metal ion would leave unpaired electron density on the oxygen. Since the donated electron density must be spin paired with the paramagnetic electrons on the metal, the unpaired electron spin left on the oxygen will be parallel to those on the metal ion. The external magnetic field produces a net component of this spin aligned with the field producing a downfield or paramagnetic shift. Experimentally Ni^{2+}, which has only completely and half filled _d_ orbitals, gives a downfield shift for the second sphere waters which is consistent with the above picture. Similar reasoning (using Hund's Rule) suggests donation by oxygens into an empty orbital should produce an upfield shift. The downfield shift for Cr^{3+} indicates that donation by the second sphere waters into the half filled t_{2g} orbitals is more effective than that into the empty Eg orbital in producing unpaired electron density on the oxygens.

Since the attraction of second coordination sphere waters to the metal ion should be almost entirely electrostatic in nature, the position of the second sphere waters is most reasonably on the center of the faces of the octrahedron formed by the first sphere waters. This position allows the closest approach between the centers of charge. Assuming the bonding orbitals of the second sphere waters are symmetric about a line joining the oxygen and metal nuclei, bonding to the t_{2g} orbitals is symmetry allowed. However bonding to the center of the faces is incompatible with the symmetry of the Eg orbital. The fact that significant donation to the Eg orbitals is observed in Ni^{2+} would lead one to the conclusion that either the waters involved are not at the center of the faces or the assumption as to axial symmetry of the oxygen orbitals is faulty. Certainly both of these reasons could contribute to the observed result. The position of the second sphere waters remains unknown, however the faces are certainly electrostatically most stable. But molecular vibrations about these positions are undoubtedly large and frequent, thereby allowing significant donation to Eg orbitals.

Electronic Relaxation Rates of Ni^{2+}

Information concerning electronic relaxation rates can be calculated from the values of $\frac{1}{T_{2m}}$ as a function of frequency. Comparison of Figs. (1) and (2) show that $\frac{1}{T_{2m}}$ is indeed a function of frequency. However straightforward calculations show that the effect is not nearly as large as would be predicted by equation (6). An arbitrary temperature of 160°C is chosen for the following calculations since this lies well into the $\frac{1}{T_{2m}}$ region for relaxation at 2 MHz. The $\frac{1}{T_{2m}}$ from Fig. (2) at this temperature inserted in equation (6) yields

$$\tau_e = 1.16 \times 10^{-11} \text{ sec}$$

Eqs. (6) and (7) can be used to estimate $\frac{1}{T_{2m}}$ at 8.134 MHz, using the above value of τ_e assuming $T_{1e} = T_{2e}$ at 2.00 MHz. If T_{1e} and T_{2e} are assumed to be frequency independent up to 8.134 MHz, equations (6) and (7) give

$$\left.\frac{1}{T_{2m}}\right|^{\text{predicted}}_{8\text{ MHz}} = 1.24 \times 10^5 \text{ sec}^{-1}$$

Experimentally $\frac{1}{T_{2m}}$ has been found to be $(1.40 \pm 0.05) \times 10^5 \text{ sec}^{-1}$. This difference lies well outside experimental error and can only be accounted for by a faulty assumption as to the frequency independence of T_{1e} and T_{2e}.

Regardless of the physical origin of the relaxation, the various theories for triplet electronic relaxation times have identical correlation time and frequency dependencies.[16,17,18]

$$\frac{1}{T_{1e}} \propto \frac{8\tau_c}{1 + 4\omega_S^2 \tau_c^2} + \frac{2\tau_c}{1 + \omega_S^2 \tau_c^2} \qquad (13)$$

$$\frac{1}{T_{2e}} \propto 3\tau_c + \frac{5\tau_c}{1 + \omega_S^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega_S^2 \tau_c^2} \qquad (14)$$

Ni^{2+} has a triplet ground state and can have only one longitudinal and one transverse relaxation time. The condition for the rigorous application of these formulas is

$$\tau_c \ll T_{1e}, T_{2e} \qquad (15)$$

The assumption that $T_{1e} = T_{2e}$ at 2.00 MHz can be stated explicitly as

$$\omega_S^2 \tau_c^2 \ll 1 \qquad (16)$$

Under these conditions a simple manipulation of equation (13) and (14) yields

$$(T_{1e})_{8\ \mathrm{MHz}} = (T_{1e})_{2\ \mathrm{MHz}}\ 10 \left[\frac{8}{1 + 4\omega_S^2 \tau_c^2} + \frac{2}{1 + \omega_S^2 \tau_c^2} \right]^{-1} \qquad (17)$$

$$(T_{2e})_{8\ \mathrm{MHz}} = (T_{2e})_{2\ \mathrm{MHz}}\ 10 \left[3 + \frac{5}{1 + \omega_S^2 \tau_c^2} + \frac{2}{1 + 4\omega_S^2 \tau_c^2} \right]^{-1} \qquad (18)$$

The τ_c can now be adjusted so that the 8 MHz T_{1e} and T_{2e} when used in Eqs. (6) and (7) give the experimental $\frac{1}{T_{2m}}$. This procedure yields

$$\tau_c = 1.1 \times 10^{-12} \text{ sec at } 160°\text{C}$$

The adequacy of the assumption (16) can now be seen to be excellent

$$\omega_S^2 \tau_c^2 = 3 \times 10^{-3}$$

The result raises the question of the validity of the calculation in that the correlation time for electronic relaxation is only a factor of five or so smaller than the relaxation time and therefore condition (15) is no longer strictly fulfilled. It seems reasonable, however, that the correlation time and frequency dependence of the relaxation time would be less sensitive to this restriction than would be the calculation of an absolute relaxation rate.

Another independent measure of this correlation time can be had by measuring the frequency dependence of the rate of relaxation of water protons in a Ni^{2+} solution. This has been done previously by Morgan and Nolle[6] for protons from 2 to 60 MHz. Their data are reproduced in Fig. (5) along with the results of the present study at 60, 100 and 220 MHz.

The application of the electronic relaxation theories developed after the work of Morgan and Nolle can account for the lack of the expected dispersion region. The frequency dependence of the T_{1e} and T_{2e} act to cancel the dispersion region of the dipolar coupling up to 60 MHz. Above this frequency the T_{1e} frequency dependence dominates and causes the linewidth to increase very sharply. The solid line in Fig. (5) is a plot of the expected dipolar frequency dependence using equation (8) and including the frequency dependence of T_{1e} and T_{2e} as predicted by equations (13) and (14). The correlation time which fits the data best is

$$\tau_c = 1.8 \times 10^{-12} \text{ sec at } 30°\text{C}$$

Extrapolating back to 160°C to compare with the previous result and using V = 1.20 kcal/mole gives

$$\tau_c = 1.0 \times 10^{-12} \text{ sec at } 160°\text{C}$$

This remarkably good agreement is, of course, coincidental considering the probable compounding of experimental errors along the way. The consistency of the two methods is gratifying under any circumstances.

All the quantities necessary to calculate the 8 MHz $\frac{1}{T_{2m}}$ as a function of temperature are now known. The results of these calculations involving equations 6, 7, 9, 17 and 18 are shown plotted in Fig. (1) as the solid curve thus designated. The line is obviously not linear. However for the purpose of fitting the T_{2p} data in Fig. (1) an effective slope in the high temperature region of 0.6 kcal/mole was used as a quite adequate approximation. The correctness of the T_{2m} calculation is verified experimentally by measurement of the bound water resonance linewidth. The values at several temperatures have been plotted as triangles in Fig. (1) and the agreement with the predicted values is good.

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Figure Captions

Figure 1. $P_m T_{2p}$ versus reciprocal of absolute temperature at 8.134 MHz for the ^{17}O NMR of aqueous solutions of $Ni(ClO_4)_2$.

o - bulk water data with line resulting from curve fitting.

△ - bound water linewidth data with curve labelled "T_{2m}" resulting from calculations as explained in the text.

Figure 2. $P_m T_{2p}$ versus reciprocal of absolute temperature at 2.000 MHz for the bulk ^{17}O NMR of aqueous solutions of $Ni(ClO_4)_2$ with the solid curve the result of curve fitting as discussed in the text.

Figure 3. $\Delta\omega_{H_2O}/P_m$ versus reciprocal of absolute temperature at 8.134 MHz for the ^{17}O chemical shift of the bulk water in aqueous solutions of $Ni(ClO_4)_2$. Curved line is the result of a calculation using equation (3) and the parameters in Table III.

o - 0.0314 M nickelous perchlorate,0.10 M perchloric acid.

△ - 0.392 M nickelous perchlorate, 0.10 M perchloric acid in a sphereical container.

Figure 4. ^{17}O NMR spectra of a 3.7 M aqueous solution of nickelous perchlorate and 0.10 M perchloric acid at 25°C. Spectrum A shows the bulk waters on the left 1.11×10^5 Hz upfield from the bound waters on the right. A is the average of 100 scans, B is an amplification of A.

Figure 5. Product of Molarity and Proton T_2 versus Proton Larmor frequency for aqueous solutions of nickelous perchlorate 0.10 M in perchloric acid at 30°.

o - data from Morgan and Nolle (Ref. 6).

△ - present work.

0 0 0 0 3 6 0 0 6 9 8

Figure 1

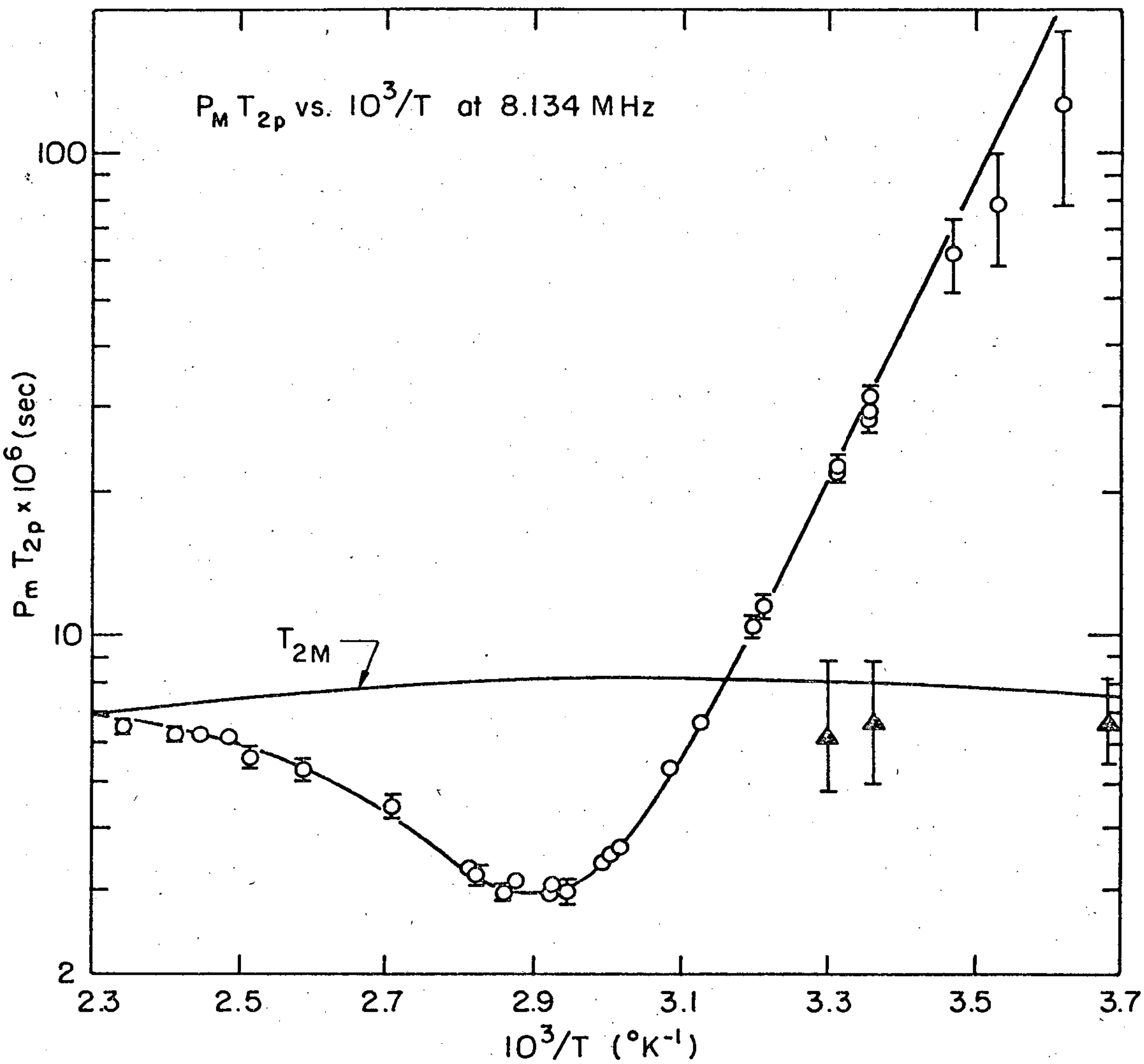

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Figure 2

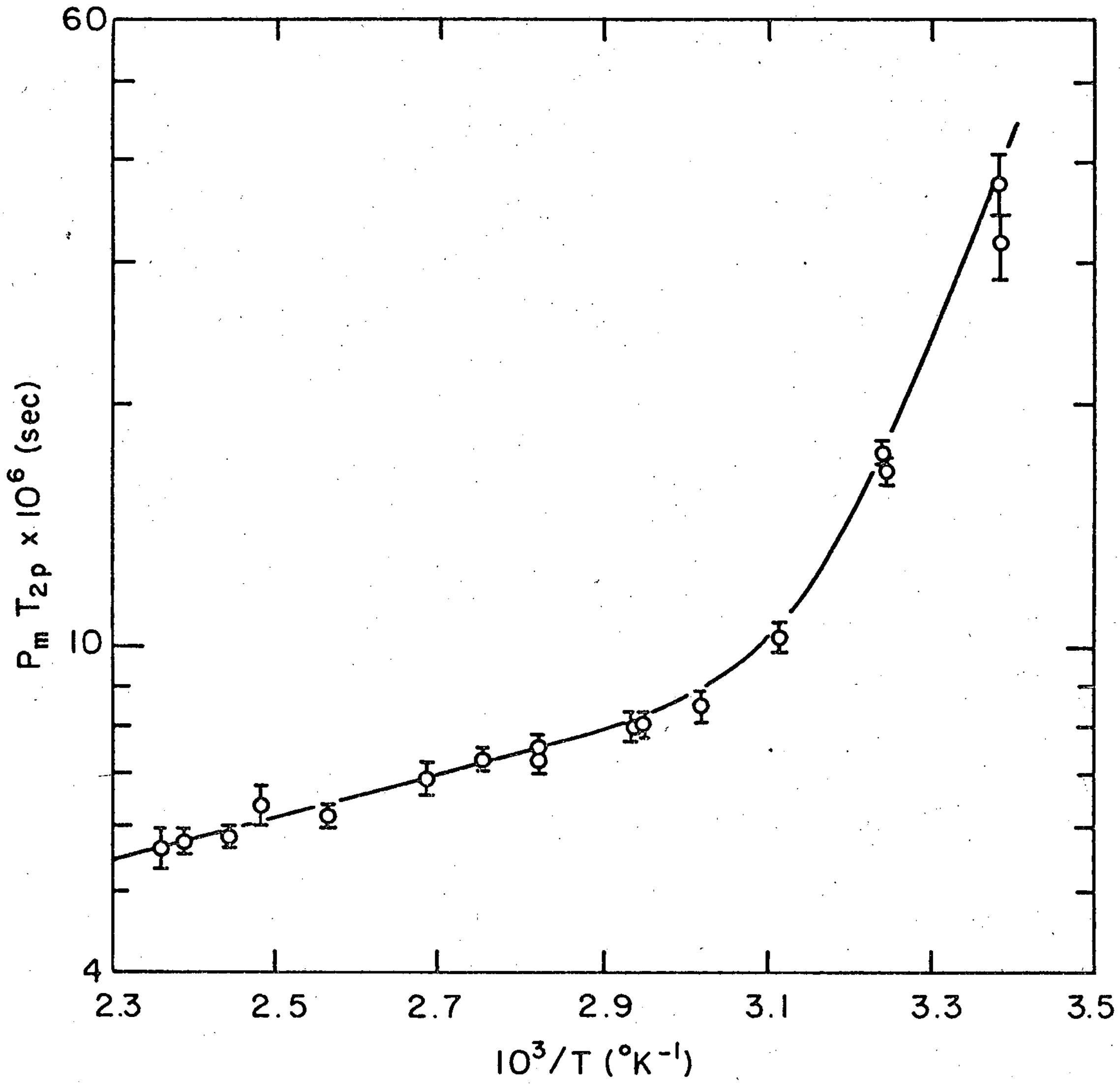

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Figure 3

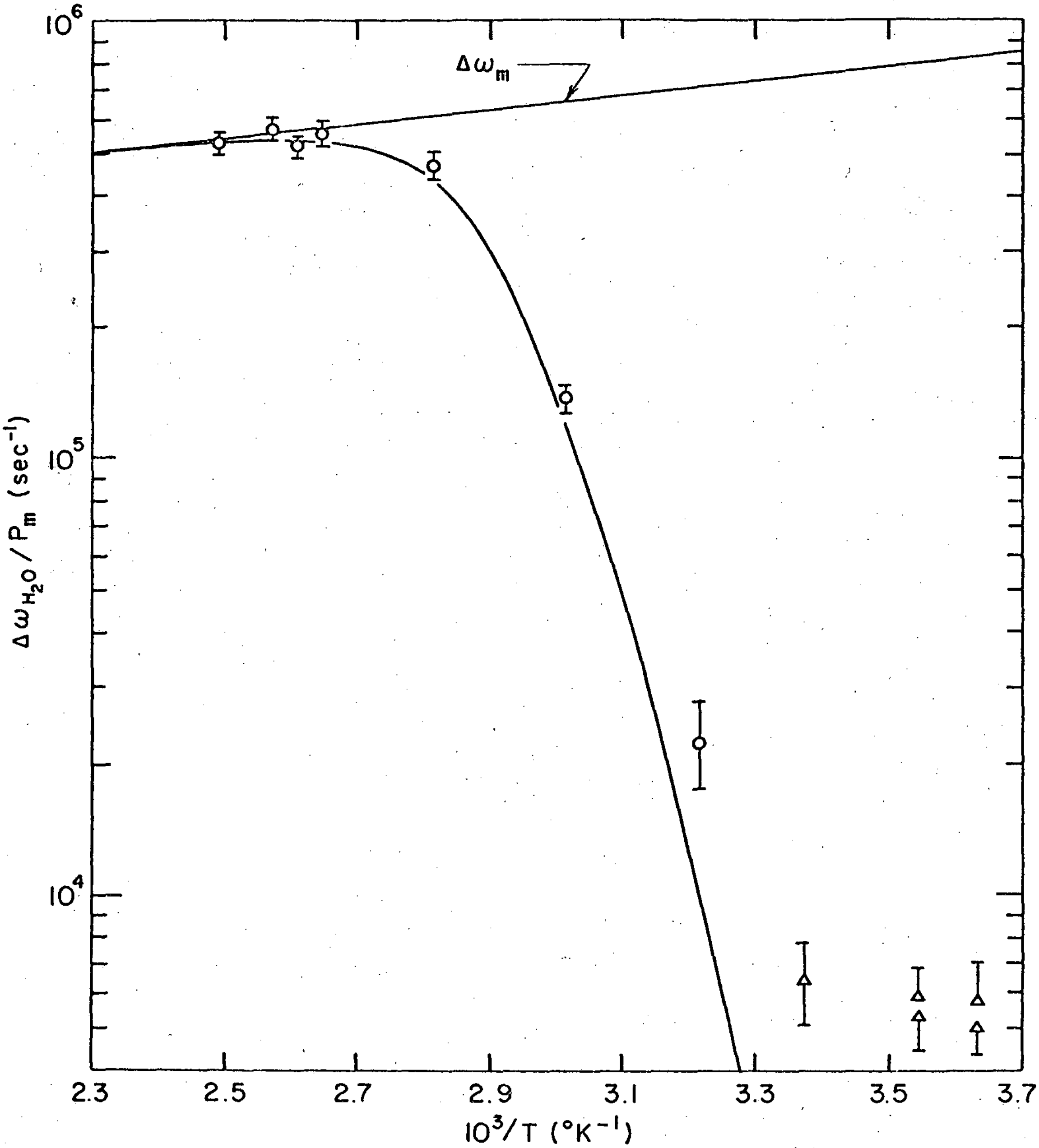

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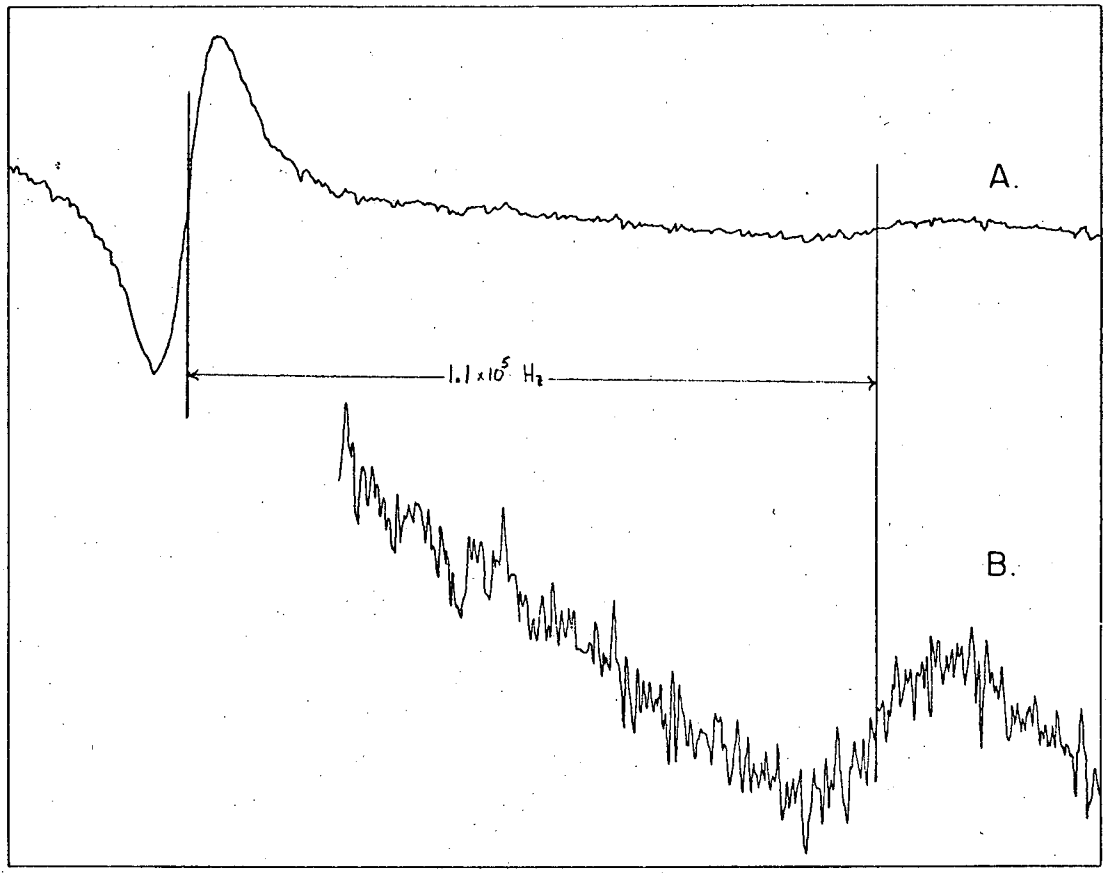
Figure 4



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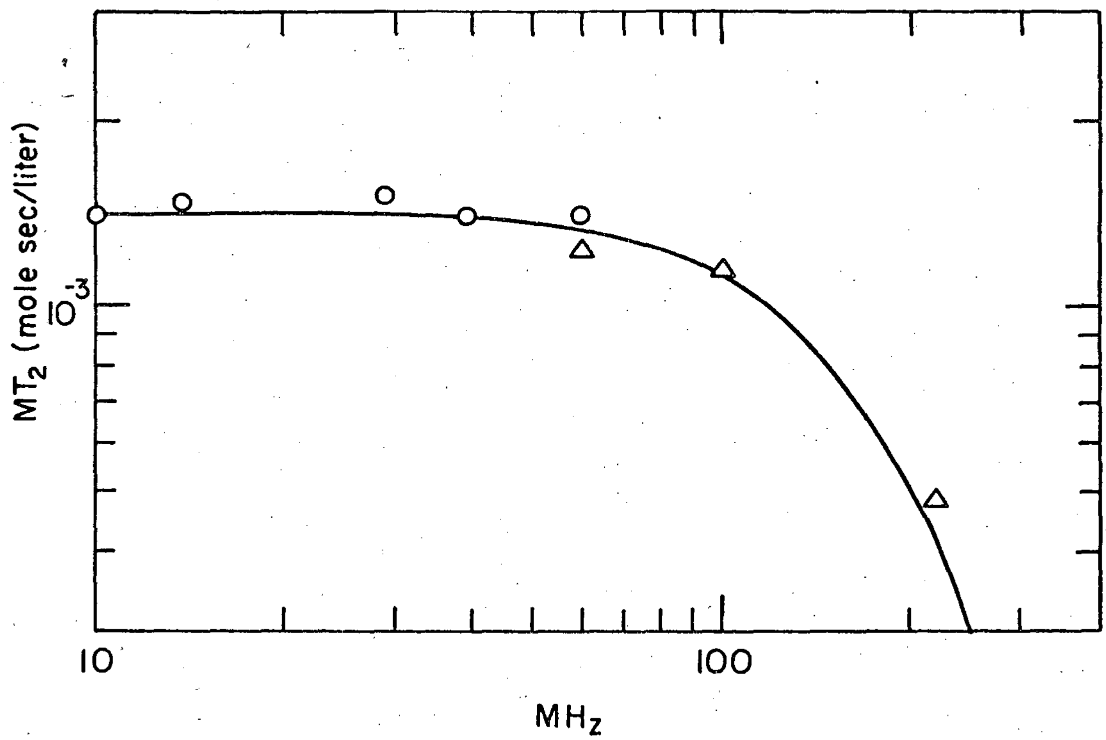

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