Oxygen-17 Magnetic Resonance Studies of the Hydration of the Ferrous and Nickelous Ions

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Abstract: The oxygen-17 magnetic resonance absorption spectra of the water molecules coordinated to ferrous and nickelous ions have been observed and studied. The hyperfine coupling constants were found to be $-(1.10 \pm 0.01) \times 10^7$ and $-(2.82 \pm 0.01) \times 10^7$ Hz for the ferrous and nickelous ions, respectively. The electron relaxation times were found to be 4.7×10^{-13} sec at $-50°$ for the ferrous ions and 5.7×10^{-12} sec at $-30°$ for the nickelous ions. The studies led to the conclusion that both the ferrous and nickelous ions are coordinated to six water molecules in aqueous solutions.

Aqueous solutions of transition metal ions reveal, under favorable conditions, nuclear magnetic resonance absorption signals due to both the bound and nonbound ligands. As is well known, the conditions required for observation of distinct signals are rarely met.[2] Previously, oxygen-17 and proton magnetic resonance spectra of water molecules coordinated to nickelous[1] and cobaltous[3] ions have been observed. In this paper we report the observation of the oxygen-17 magnetic resonance spectrum of the water molecules coordinated to ferrous ions (Figure 1) and the observation and extension of the oxygen-17 magnetic resonance studies of the hydration of nickelous ions (Figure 2).

X-Ray studies of some of the nickelous hydrate salts revealed distortion from octahedral symmetry in the solid state[4–6] and in aqueous solutions.[7] The splitting of the main bands of the absorption spectra of the hepta and the hexa solid hydrates of $NiSO_4$[8] has also been interpreted in terms of distortion from octahedral symmetry. It is, however, generally accepted that nickelous ions are not susceptible to the Jahn–Teller effect and that, therefore, no marked distortion from octahedral symmetry should be observed. In particular, the complex $[Ni(H_2O)_6]^{2+}$ is considered a quite regular octahedron,[9] ${}^3A_{2g}$ being its ground state, and hence not susceptible to the Jahn–Teller effect.

It appeared, therefore, to be of much interest to extend the previous studies and if possible confirm the conclusions mentioned above by other physical methods. It would also be of value to study the effect of the distortion as it may be manifested in the kinetic and thermodynamic parameters and the hyperfine coupling constants of the axial and equatorial water molecules.

The direct observation of the oxygen-17 magnetic resonance absorption signal of the water molecules coordinated to the nickelous paramagnetic ion[2] opened the way for these studies. The hyperfine coupling constant between the oxygen-17 nuclei and the nickelous ion unpaired electrons was calculated from the chemical shift between the coordinated and noncoordinated water molecules. The temperature dependence of the oxygen-17 transverse relaxation times of the bulk water of aqueous solutions of nickelous perchlorate salts has suggested that the relaxation effects are due to four water molecules and therefore either the nickelous ion is tetrahedrally coordinated or distortion from octahedral symmetry exists.[2] In a more recent paper,[10] oxygen-17 magnetic resonance studies of the chemical shifts of the bulk water of aqueous solutions of nickelous perchlorate salt also suggested that the distortion from octahedral symmetry of the nickelous ion complex is manifested in the hyperfine coupling constant and in the rate of exchange of the water molecules surrounding the nickelous ion.

In the present study the previous measurements have been repeated with water more highly enriched in oxygen-17 as it became available from the separation plant at the Weizmann Institute of Science. The measurements have been extended to higher temperatures, allowing more accurate determination of the previously determined parameters.[2,10]

Basic Equations

The equations relevant for the interpretation of our results were summarized in a previous paper[11] and the same notation will be used here. For the benefit of the readers and easy reference, the most relevant equations will be given here.

The contributions of the dipolar and scalar interactions to the transverse relaxation rate of a nucleus due to its interaction with unpaired electrons are given by eq 1 and 2, respectively, where the symbols have their usual meaning[2]

$$\left(\frac{1}{T_{2M}}\right)_{DD} = \frac{1}{15} S(S+1) \frac{\hbar^2 \gamma_e{}^2 \gamma_n{}^2}{r^6} \times \left\{4\tau_1 + \frac{\tau_2}{1 + (\omega_n - \omega_e)^2 \tau_2{}^2} + \frac{3\tau_1}{1 + \omega_n{}^2 \tau_1{}^2} + \frac{6\tau_2}{1 + \omega_e{}^2 \tau_2{}^2} + \frac{6\tau_2}{1 + (\omega_n + \omega_e)^2 \tau_2{}^2}\right\} \quad (1)$$

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(1) (a) The Weizmann Institute of Science; (b) Argonne National Laboratory; on leave from the Weizmann Institute of Science.

(2) R. E. Connick and D. Fiat, *J. Chem. Phys.*, **44**, 4103 (1966).

(3) (a) D. Fiat, Z. Luz, and B. L. Silver, *ibid.*, **49**, 1376 (1968); (b) N. A. Matwiyoff and P. E. Darley, *J. Phys. Chem.*, **72**, 2659 (1968).

(4) J. H. Van Vleck, *Phys. Rev.*, **41**, 208 (1932).

(5) P. L. Mukherjee, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **91**, 504 (1935).

(6) L. Pauling, *ibid.*, **72**, 345 (1930).

(7) A. K. Dorosh and A. F. Skryshevskiĭ, *Zh. Strukt. Khim.*, **5**, 911 (1961).

(8) H. Hartmann and H. Miller, *Discuss. Faraday Soc.*, **26**, 49 (1958).

(9) M. H. L. Pryce, *ibid.*, **26**, 21 (1958).

(10) D. Fiat and A. M. Chmelnick, *Proc. Colloq. AMPERE (Magn. Resonance Relaxation), 1966*, **14** 1157 (1967).

(11) A. M. Chmelnick and D. Fiat, *J. Chem. Phys.*, **51**, 4238 (1969).

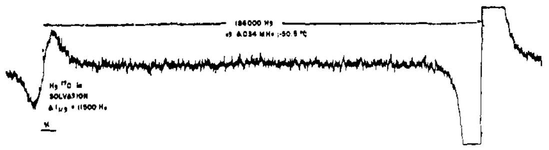

Figure 1. Oxygen-17 spectrum of ferrous perchlorate aqueous solution.

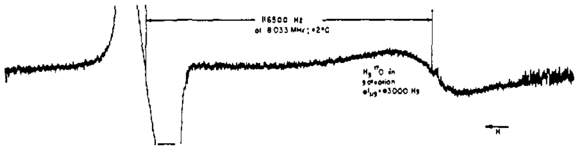

Figure 2. Oxygen-17 spectrum of nickelous perchlorate aqueous solution.

$$\left(\frac{1}{T_{2\mathrm{M}}}\right)_{\mathrm{SC}} = \frac{1}{3}\left(2\pi\frac{A}{h}\right)^2 S(S+1) \times \left\{\tau_1 + \frac{\tau_2}{1 + (\omega_\mathrm{n} - \omega_\mathrm{e})^2\tau_2{}^2}\right\} \quad (2)$$

and where A/h is the hyperfine coupling constant given in hertz.

The chemical shift of the solvent due to the presence of the paramagnetic ions and under conditions of fast exchange, $\Delta\omega_\mathrm{a}$, is related to the chemical shift between the coordinated ligands under conditions of slow exchange and the coalescent signal under conditions of fast exchange, $\Delta\omega_\mathrm{M}$, by the following equation[12]

$$\Delta\omega_\mathrm{a} = -\Delta\omega_\mathrm{M}P_\mathrm{M} \quad (3)$$

where P_M is the ratio of the coordinated and noncoordinated ligands.

The chemical shift between the coordinated and noncoordinated ligands, $\Delta\omega_P$, is given by

$$\Delta\omega_P = \Delta\omega_\mathrm{a}[1 + (1/P_\mathrm{M})] \quad (4)$$

and the hyperfine coupling constant A may be calculated from the following relation[13]

$$\Delta\omega_P/\omega = -S(S + 1)(\gamma_\mathrm{e}/\gamma_\mathrm{N})(A/3kT) \quad (5)$$

The enthalpy and entropy of activation ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively) may be calculated from the following equation[14]

$$\tau_\mathrm{M} = (h/kT)\exp(\Delta H^{\ddagger}/RT - \Delta S^{\ddagger}/R) \quad (6)$$

where τ_M is the mean lifetime of the coordinated ligands.

Experimental Section

Ferrous Ion. A ferrous perchlorate solution of composition $X_{\mathrm{Fe}^{2+}} = 0.05$ (where X_M gives the ratio of the number of solute molecules to the number of solvent molecules) was prepared by dissolving anhydrous ferrous sulfate (obtained from Fischer Scientific Co.) in acidified water enriched to 25 atom % in oxygen-17 obtained from the Heavy Oxygen Plant of the Weizmann Institute. The perchloric acid used was obtained from Fluka ($X_{\mathrm{HClO}_4} = 0.0078$). The sulfate ions were precipitated by barium perchlorate (obtained from G. Frederick Smith Chemical Co.).

A Varian DP-60 spectrometer operating at 8.034 MHz with the variable-frequency unit (V 4210 A) was used. The spectra were recorded by the derivative method, and line widths were corrected for modulation broadening.[15] Temperature changes were effected by passing cooled nitrogen through the annular space between the sample cell and a dewar. The temperatures were measured by inserting a glass capillary containing a copper–constantan thermocouple into the solution during the measurements. The temperatures were kept constant to within ±0.5° and read on a Leeds and Northrup temperature potentiometer.

The frequency was read using a counter–timer, Monsanto Model 101 B, the counter being connected to the transmitter throughout the measurement. Nonlinearity effects of the field sweep were eliminated using the following procedure: a signal of enriched water was observed at 8.034 MHz and then at a frequency lowered by 170,000 Hz. Previously,[2] the chemical shift between the coordinated and noncoordinated water molecules was calculated assuming linearity of the sweep and by interpolation between oxygen-17 and deuterium resonances.

It has been found that no special precautions need be taken in order to avoid small amounts of ferric ions which may be present in the solution. This point will be discussed in more detail later.

Nickelous Ion. The following solutions were prepared and studied. (1) A nickelous perchlorate solution of composition $X_{\mathrm{Ni}^{2+}} = 0.0576$ was prepared by dissolving dried nickelous chloride (obtained from BDH) in acidified water (30 atom % in oxygen-17, $X_{\mathrm{HClO}_4} = 0.00534$). The chloride ions were precipitated using dried silver perchlorate (obtained from BDH). Measurements at various temperatures were made as described in the previous section. (2) A nickelous perchlorate solution of composition $X_{\mathrm{Ni}^{2+}} = 0.00287$, $X_{\mathrm{HClO}_4} = 2 \times 10^{-4}$, and $X_{(\mathrm{CH}_3)_2\mathrm{O}} = 0.0411$ (acetone was used as an internal reference) was prepared in a similar way.

The more concentrated solution (1) was used for the direct observation of the oxygen-17 signal of the coordinated water molecules using the Varian variable-frequency rf unit. The temperature dependence of the oxygen-17 chemical shift of the bulk water between 0 and 201° was studied with the more dilute solution (2). The Varian fixed-frequency unit (8.13 MHz) was used and the field was stabilized with the Varian Super Stabilizer.

The results at high temperatures were consistent over a period of 2 weeks, indicating the absence of irreversible reactions in the solution.

Oxygen-17 magnetic resonance studies of the acidified acetone solution were made prior to the addition of the nickelous salt and repeated after adding the salt.

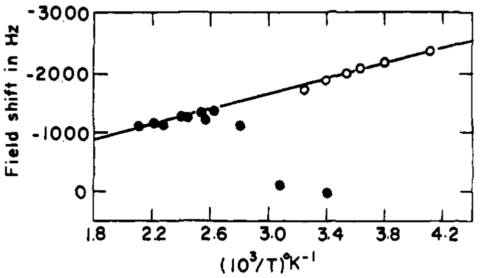

Figure 3. Chemical shift temperature dependence of bound and unbound water molecules in nickelous perchlorate solution: (○) bound molecules, $X_{\mathrm{Ni}^{2+}} = 5.76 \times 10^{-2}$, $X_{\mathrm{HClO}_4} = 5.34 \times 10^{-3}$; (●) unbound molecules, $X_{\mathrm{Ni}^{2+}} = 2.87 \times 10^{-3}$, $X_{\mathrm{HClO}_4} = 2 \times 10^{-4}$, $X_{(\mathrm{CH}_3)_2\mathrm{CO}} = 4.11 \times 10^{-2}$. Data of bound molecules were converted to the concentration of unbound ones.

Results

Nickelous Ion. The chemical shift temperature dependence of the bound water is given in Table I. The data have been converted to bulk shift (eq 3) assuming a coordination number of 6.0. These results are shown together with the bulk shift data in Figure 3. The deviations at high temperatures from the solid line are due to the exchange between the coordinated and noncoordinated molecules.

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(12) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962); **41**, 2553 (1964).

(13) N. Bloembergen, *ibid.*, **27**, 595 (1957).

(14) H. Eyring, *Chem. Rev.*, **17**, 65 (1935).

(15) H. Wahlquist, *J. Chem. Phys.*, **35**, 1208 (1961).

Table I. Chemical Shifts and Line Widths of Bound Water

	Temp, °C	Chemical shift, Hz	Line width, Hz
Ferrous perchlorate	−22	159,000	65,000
	−29	165,800	31,000
	−39	176,500	16,000
	−50.5	186,000	11,400
Nickelous perchlorate	35	97,000	49,000
	21	106,200	39,000
	10	112,400	43,000
	2	116,700	43,000
	−10	122,500	50,000
	−29.5	133,500	51,000

The hyperfine coupling constant was calculated from the slope of the solid line (eq 4 and 5) and found to be $-(2.82 \pm 0.01) \times 10^7$ Hz. The line widths of the solvation shell signals are given in Table I. The longitudinal relaxation time of the unpaired electrons was calculated from the line widths of the solvation shell as described previously.[2] The contribution of the exchange of the water to the line widths of the solvation shell was calculated (eq 6) using the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values given in ref 2. The contribution of the quadrupole interaction to the line width of the solvation shell[11] would be within the limits of experimental error.

The longitudinal relaxation time of the unpaired electrons at −29.5° (eq 1 and 2) was found to be 7.6×10^{-12} sec, assuming $T_{1e} \gg T_{2e}$, and 5.7×10^{-12} sec, assuming $T_{1e} = T_{2e}$.

Ferrous Ion. The chemical shift temperature dependence of the oxygen-17 signal in the solvation shell is given in Table I. These results are shown in Figure 4. The solid line has been drawn assuming zero shift at infinite temperature. The deviations from the line of the high-temperature data are attributed to the exchange effect. The hyperfine coupling constant was calculated by eq 5 and found to be $-(1.10 \pm 0.01) \times 10^7$ Hz. The line widths of the solvation shell signals are given in Table I. The longitudinal relaxation time was calculated for −50° as described in the previous section. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were taken from ref 12. T_{1e} was found to be 3.7×10^{-12} sec, assuming $T_{1e} \gg T_{2e}$, and 4.7×10^{-13} sec, assuming $T_{1e} = T_{2e}$.

Previously,[12] the oxygen-17 chemical shift of 6.17×10^{-2} *M* aqueous solution of $Fe(NH_4)_2(SO_4)_2$ at 300°K was determined and found to be 119 ppm. Within the limits of experimental error, this result is in good agreement with the present findings (Figure 4). The conversion from the data of ref 12 to those of Figure 4 was carried out by means of eq 4, assuming that the hydration number of the ferrous ion in aqueous solution is six.

Discussion

The present study shows conclusively that the hydration number of the nickelous ion in aqueous solutions is six. However, it is of vital significance to remember that this does not invalidate the conclusions arrived at by other physical methods, since the time scales of the different methods are not the same. It may well be that the distortion from octahedral symmetry does not affect the oxygen-17 magnetic resonance spectrum, since the effects observed may represent an average over the six water molecules. The other methods may detect the effects over a much shorter period of time, that is, shorter than the time at which averaging of the effects occurs.

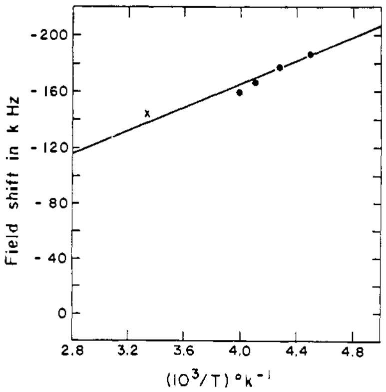

Figure 4. Chemical shift temperature dependence of bound ligands in a ferrous perchlorate solution. × represents a chemical shift of the bulk taken from ref 12 and converted to the chemical shift of bound molecules.

It is striking that within the limits of experimental error the present results are in agreement with the previous ones. The major reason for the different conclusion is that in the previous study of oxygen-17 chemical shifts of the bulk were measured in the temperature range 0–100°. This limited range did not allow definite conclusions to be drawn from the chemical shift behavior as a function of temperature. Moreover, the calibration technique used here, the higher oxygen-17 concentration, and the internal reference method used for the bulk shift measurements render the present results more accurate than the previous ones. Thus, the results shown in Figure 3 seem to be consistent with a coordination number of six for the nickelous ion over the temperature range −30 to +200°.

The hydration of the nickelous ion was studied previously by means of the flow adaptation of the isotopic dilution method,[16] and the lifetime of the molecule in the sphere of hydration was found to be less than 10^{-2} sec at 25°, in agreement with the nuclear magnetic resonance studies. However, the hydration number of the nickelous ion was not determined by this method.

The hydration of the nickelous ion was studied more recently by proton magnetic resonance[17] and measurements of line widths and integration of the bulk signal led to the conclusion that the coordination number is six at −30°.

The oxygen-17 measurements of the ferrous ion aqueous solution have been extended to very low temperatures. The effects of the small amounts of ferric ions which may be present in the solution are negligible owing to the long constant characterizing the ferrous–ferric[18] transfer reaction. On the other hand, small amounts of ferric ions can severely affect the results of the fast-exchange region, especially at high temperatures.[12] The value given in the literature[12] for the bulk chemical shift is in agreement with and within 4% of our results assuming that the ferrous ion is hexacoordinated in aqueous solution. Spectroscopic measurements[19] have led to similar conclusions.

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(16) H. W. Baldwin and H. Taube, *J. Chem. Phys.*, **33**, 206 (1960); J. P. Hunt and H. Taube, *ibid.*, **18**, 757 (1950).

(17) T. J. Swift and G. P. Weinberger, *J. Amer. Chem. Soc.*, **90**, 2023 (1968).

(18) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

(19) W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, **3**, 1295 (1964).