DEPENDENCE OF THE NUCLEAR RELAXATION RATE ON THE SYMMETRY OF THE Ti^{3+} COMPLEX IN AQUEOUS SOLUTIONS

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Abstract

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DEPENDENCE OF THE NUCLEAR RELAXATION RATE ON THE SYMMETRY OF THE Ti^{3+} COMPLEX IN AQUEOUS SOLUTIONS

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One of the authors has investigated the temperature and acid dependences of the relaxation rates of the longitudinal $T_{\parallel}^{-1}$ and transverse $T_{\perp}^{-1}$ components of the vector of nuclear magnetization $\mathbf{M}$ of protons in aqueous solutions of the ions Ti^{3+}, Mn^{2+}, and Cr^{3+}.

It was shown that, according to the theory (^{1}), in the case of Ti^{3+}, both in the symmetric $[\mathrm{Ti(H_2O)_6}]^{3+}$ (I) and in the asymmetric $[\mathrm{TiF}_n(\mathrm{H_2O})_{6-n}]^{(3-n)+}$, $n \neq 6$ (II), complexes, the relaxation rate of the longitudinal component $T_{\parallel}^{-1}$ is determined by the correlation time of the dipole-dipole interaction proton—ion. The contribution of the contact $A\,\mathbf{IS}$ interaction to the longitudinal relaxation time $T_{\parallel}$ is much smaller than the dipole-dipole contribution.

The relaxation rate of the transverse component $T_{\perp}^{-1}$ is determined by the contribution to the relaxation from contact interactions (CI):

$$\left(\frac{1}{T_{\perp}}\right)_{\mathrm{CI}} = \frac{P_{\mathrm{B}}}{T_{\perp\mathrm{B}}} = \frac{N_S m A^2 S(S+1)}{3N_I \hbar^2(\tau_{\mathrm{B}}^{-1} + T_1^{-1})}. \tag{1}$$

Here N_S, N_I are the concentrations of paramagnetic atoms and protons in the solution, respectively; τ_{B} is the lifetime of a water molecule (protons) in the first coordination sphere of the paramagnetic atom; m is the coordination number; T_1 is the spin-lattice relaxation time of the electron spin; A is the constant of the contact interaction.

Denoting in formula (1) the constant quantities

$$\frac{N_S m S(S+1)}{3N_I \hbar^2} = C,$$

formula (1) may be rewritten in the following form:

$$\left(\frac{1}{T_{\perp}}\right)_{\mathrm{CI}} = \frac{CA^2}{\tau_{\mathrm{B}}^{-1} + T_1^{-1}}. \tag{2}$$

Fig. 1. Dependence of the nuclear relaxation rates $T_{\parallel}^{-1}$, $T_{\perp}^{-1}$, and of the e.p.r. signal amplitude on the ratio N_F/N_{Ti}. $N_{\mathrm{Ti}} = 0.15$ mol/l for NaF and $N_{\mathrm{Ti}} = 0.9$ mol/l for HF

Figure 1: Fig. 1. Dependence of the nuclear relaxation rates $T_{\parallel}^{-1}$, $T_{\perp}^{-1}$, and of the e.p.r. signal amplitude on the ratio N_F/N_{Ti}. $N_{\mathrm{Ti}} = 0.15$ mol/l for NaF and $N_{\mathrm{Ti}} = 0.9$ mol/l for HF

In addition, from the dependence of the relaxation time $T_{\perp}$ on the acidity of the medium for Ti^{3+}, the relation $\tau_{\mathrm{B}}^{-1} < T_1^{-1}$ was obtained. Then formula (2) may be written in its final form as

$$\left(\frac{1}{T_{\perp}}\right)_{\mathrm{CI}} = CA^2T_1. \tag{3}$$

It follows from formula (3) that the relaxation rate $T_{\perp}^{-1}$ is determined by the spin-lattice relaxation time of the electron spin T_1 and by the constant of the contact interaction A.

It is known (^{2}) that for paramagnetic ions with an orbital moment not equal to zero, the relaxation time T_1 increases with increasing orbital splitting caused by an electric crystalline field of low symmetry. The magnitude of this splitting is the greater, the larger the low-symmetry component.

The EPR signal in solutions of Ti^{3+} in symmetric complexes I at room temperature is not observed because of the short T_1 (small splitting). In asymmetric complexes II, the EPR line at room temperature has a width $\delta H \sim 18$ oersted (^{3}).

In nuclear magnetic resonance, according to (3), an increase or decrease in the symmetry of the complex should manifest itself in a change in the transverse relaxation time $T_{\perp}$.

We measured the dependence of the nuclear relaxation rate $T_{\parallel}^{-1}$ (Fig. 1, curves 1, 2) and $T_{\perp}^{-1}$ (curves 3, 4), as well as the e.p.r. signal amplitude for complex II at various values of the ratio $\frac{N_F}{N_{\mathrm{Ti}}}$, where N_F and N_{Ti} are the concentrations of fluorine and titanium, respectively. The nuclear resonance measurements were carried out on a spin-echo apparatus (4), and the e.p.r. signal on a standard EPR-2 spectrometer at room temperature at frequencies $\nu = 16.365$ MHz and $\nu = 9320$ MHz, respectively. From curves (1) and (2) we see that, with increasing ratio N_F/N_{Ti}, the relaxation rate $T_{\parallel}^{-1}$ decreases. This becomes understandable if one takes into account that the rate of modulation of the proton–brown ion

Fig. 1. Dependence of the nuclear relaxation rates $T_{\parallel}^{-1}$, $T_{\perp}^{-1}$, and of the e.p.r. signal amplitude on the ratio N_F/N_{Ti}. $N_{\mathrm{Ti}} = 0.15$ mol/l for NaF and $N_{\mathrm{Ti}} = 0.9$ mol/l for HF.

dipole-dipole interaction by Brownian rotation of the complex is much greater than the rate of modulation by relaxation of the electron spin, and the electron relaxation does not affect the measured values of $T_{\parallel}^{-1}$. This is true even in the case of symmetric complexes, where the electron time is shorter than in asymmetric ones (5). Obviously, the decrease in the relaxation rate $T_{\parallel}^{-1}$ with increasing ratio N_F/N_{Ti} is caused by a decrease in the probability of finding water molecules in the first coordination sphere due to replacement of part of the coordinated H_2O molecules by fluorine ions. The increase in the relaxation rate $T_{\perp}^{-1}$ (curves 3, 4) and in the e.p.r. signal amplitude (curve 5) with increasing ratio N_F/N_{Ti} is explained by us as a lengthening of the electron-spin relaxation time T_1 as a result of an increase in the low-symmetry component of the electric field of the ligands acting on the Ti^{3+} ion when the composition of the complex changes. Obviously, the maximum of the e.p.r. signal amplitude corresponds to the maximum content of complex ions of low-symmetry structure, which should possess the longest time of paramagnetic relaxation T_1. A further increase in the ratio N_F/N_{Ti} apparently leads to an increase

symmetry of the complex (formation of $[\mathrm{TiF}_6]^{3-}$ complexes), as a result of which the amplitude of the EPR signal decreases $^{(6)}$.

It is seen from Fig. 1 that the positions of the maxima for the relaxation rate $T_{\perp}^{-1}$ and for the intensity of the EPR signal approximately coincide. This indicates the existence of proportionality $T_{\perp}^{-1} \sim T_1^{-1}$ (see formula (3)). We note that the relaxation rate $T_{\perp}^{-1}$ passes through a maximum somewhat earlier, at values $N_F/N_{\mathrm{Ti}} \simeq 3$, which may be due to two reasons: a decrease in the probability of finding water molecules in the first coordination sphere as a result of replacement of water molecules by F^- ions, and exchange interactions between oppositely charged paramagnetic ions $[\mathrm{TiF}_2(\mathrm{H}_2\mathrm{O})_4]^+$, $[\mathrm{TiF}_4(\mathrm{H}_2\mathrm{O})_2]^-$, $[\mathrm{TiF}_6]^{3-}$, $[\mathrm{Ti}(\mathrm{H}_2\mathrm{O})_6]^{3+}$ $^{(7)}$. Similar results (as for NaF) were obtained for solutions upon addition of KF. The stronger increase in the relaxation rate $T_{\perp}^{-1}$ for HF (see curve 3) is caused by an increase in the acidity of the solution as the ratio N_F/N_{Ti} is increased. To confirm the assumption concerning the formation of complexes (II), we measured the effectiveness of the influence of Ti^{3+} on the relaxation times of F^{19} in hydrofluoric acid.

It is known $^{(8)}$ that, in the case of rapid chemical exchange between F^- ions present in the solution and in the first coordination sphere of a paramagnetic atom, a strong effectiveness of paramagnetic atoms in shortening the nuclear relaxation times of F^{19} in HF is observed; in this case the ratio $(N_S T_{\parallel})_H / N_S (T_{\parallel})_F$ reaches values $\sim 10^2$. For the Ti^{3+} ion we obtained the ratio $(N_S T_{\parallel})_H / (N_S T_{\parallel})_F = 4$, which indicates slow exchange between F^- ions in the solution and in the first coordination sphere. When the temperature of the solution is raised from 20 to 40°, fluorine exchange increases; at the same time, as was to be expected, the relaxation rates of the longitudinal $(T_{\parallel}^{-1})_F$ and transverse $(T_{\perp}^{-1})_F$ components of the nuclear magnetization vector increase.

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