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Abstract

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TEMPERATURE DEPENDENCE OF THE NUCLEAR MAGNETIC RELAXATION TIMES OF PROTONS AND DEUTERONS IN AQUEOUS SOLUTIONS OF Mn^{2+} IONS

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In papers ([1,2]), from experiments on the nuclear magnetic relaxation of protons, the residence time of protons τ_H in the first hydration sphere of the Mn^{2+} ion in aqueous solution was determined. The value obtained, τ_H (300° K) $\simeq 2\cdot 10^{-8}$ sec, was attributed to the mechanism of chemical exchange between the protons of the hydration shell of the ion and the protons of the rest of the solvent. However, comparison of this value of τ_H with the upper limit of the residence time of water molecules in the hydration shell ([3,4]) made it possible to suppose that the protons leave the hydration sphere of the ion as part of a water molecule.

To clarify which of the mechanisms mentioned is actually effective, we undertook a comparative study of the temperature dependence of the NMR time of protons and deuterons in aqueous solutions of Mn^{2+} ions. For this purpose, by the spin-echo method, the longitudinal T_1 and transverse T_2 relaxation times of both isotopes of hydrogen were measured. Proton resonance at a frequency of 28.7 MHz and deuteron resonance at a frequency of 4.4 MHz were observed in the same constant magnetic field of strength 6730 oersted. T_2 was determined using a sequence of 90—180° pulses, and T_1 correspondingly by 90—180—90—180° radio-frequency pulses. The temperature of the samples was varied in the interval from ~ 20 to ~ 130° C by a stream of heated air and was measured with a thermocouple attached to the wall of the sealed ampoule containing the sample. The accuracy of the measurements was: $T_{2\mathrm{H}} \sim 5\%$, $T_{2\mathrm{D}} \sim 7\%$, $T_{1\mathrm{H}} \sim 10\%$, $T_{1\mathrm{D}} \sim 12\%$, and of temperature ~ 1.5° C. Here and below the subscript H refers to the proton, and D to the deuteron.

In all experiments the same sample was used, consisting of a 0.1 M solution of $\mathrm{MnSO_4}$ in a mixture of 50% $\mathrm{H_2O}$ + 50% $\mathrm{D_2O}$. It turned out that the isotopic composition of the solvent does not affect the relaxation times, whereas in solutions of VO^{2+} ions this influence is significant ([5]). A correction for nuclear quadrupole relaxation was introduced into the obtained values of the times $T_{1\mathrm{D}}$, for which the temperature dependence of $T_{1\mathrm{D}}$ in the pure solvent was measured. The results of measurements of the NMR times are presented in Fig. 1.

From the experimental data we can obtain the values of τ_H and τ_D (^{1}). Let us turn to the equations for the NMR times in solutions of paramagnetic salt ions:

$$(1/T_1) = (1/T_1)_{\mathrm{dd}} + (1/T_1)_{\mathrm{exch}}; \tag{1}$$

$$(1/T_2) = (1/T_2)_{\mathrm{dd}} + (1/T_2)_{\mathrm{exch}}. \tag{2}$$

The first terms on the right-hand sides of the equations describe relaxation caused by the dipole-dipole magnetic interaction between paramagnetic ions and the H or D nuclei of the solvent. As is known (^{1}), the dipole-dipole contributions to the times T_1 and T_2 are approximately equal. The second terms are due to the scalar $\mathrm{A \cdot I \cdot S}$ exchange interaction (^{6}). The contribution $(1/T_1)_{\mathrm{exch}}$ to $1/T_1$ is negligibly small at the ordinarily used values of the magnetic-field strength, whereas $(1/T_2)_{\mathrm{exch}}$ gives the main contribution to transverse relaxation in aqueous solutions of Mn^{2+} ions. Taking $(1/T_1)_{\mathrm{dd}} =$ $-(1/T_2)_{\mathrm{dd}}$ and assuming $(1/T_1)_{\mathrm{dd}} \gg (1/T_1)_{\mathrm{ex}}$, from (1) and (2) we find:

$$(1/T_2)_{\mathrm{ex}} = (1/T_2) - (1/T_1). \tag{3}$$

On the other hand, the exchange contribution to T_2 can be expressed in the form $^{(1)}$:

$$(1/T_2)_{\mathrm{ex}} = \frac{1}{3} S(S+1)(Nn/\mathfrak{N})(A/h)^2 \tau_l, \tag{4}$$

where S is the spin of the Mn^{2+} ion, $S = 5/2$; N is the molar concentration of paramagnetic ions in the solution, n is the number of water molecules in the first hydration layer around the ion, $\mathfrak{N}$ is the molar concentration of water molecules, A is the exchange-interaction constant, and τ_l is the correlation time of the exchange interaction. We assume that protons and deuterons have equal probability of entering the first hydration shell. The $A \cdot I \cdot S$ interaction may be disrupted because the relaxing nuclei leave the first hydration shell, or as a result of reorientation of the spin of the paramagnetic ion caused by electronic relaxation. In general form one may write

$$(\tau_l)^{-1} = (\tau_s)^{-1} + (\tau_{\mathrm{n}})^{-1}, \tag{5}$$

where τ_s is the electronic relaxation time and τ_{n} is the residence time of hydrogen nuclei in the first hydration shell around the ion.

Fig. 1. Temperature dependence of the times of NMR in a solution of Mn^{2+} ions: a–$NT_{2\mathrm{H}}$, b–$NT_{1\mathrm{H}}$, v–$NT_{2\mathrm{D}}$, g–$NT_{1\mathrm{D}}$ in a mixture of 50% H_2O + 50% D_2O. For comparison, $NT_{2\mathrm{H}}$ in 100% H_2O are shown: our data (d), data of Gutovsky et al. (1) (e), Blumbergen and Morgan (2) (zh); $NT_{2\mathrm{D}}$ (z), $NT_{1\mathrm{D}}$ (i) in $\sim$ 100% D_2O, data of Laukien and Noack (18).

Figure 2 shows the temperature dependence of the exchange contributions to the transverse relaxation times of protons and deuterons, calculated from the experimental data (Fig. 1) by formula (3). It is evident from this figure that $(NT_{2\mathrm{H}})_{\mathrm{ex}}$ and $(NT_{2\mathrm{D}})_{\mathrm{ex}}$ vary identically with temperature and differ only in their absolute magnitudes.

As in works (1,2), we assumed that at low temperatures the correlation time of the $A \cdot I \cdot S$ interaction is determined mainly by the electronic relaxation time τ_s, while the contribution from τ_{n} amounts to only a few percent, i.e. $\tau_l \simeq \tau_s$. The electronic relaxation times can be calculated from the values published by Nolle and Morgan (7) for the EPR linewidths of Mn^{2+} ions in an aqueous (H_2O) solution. Then, taking from (7) the value $\tau_s = 3.1 \cdot 10^{-9}$ sec at 20°C and taking into account that the EPR linewidth does not change upon going from light to heavy water,* one can obtain, according to (4) and (5), the following values of the constants:

$$(A_{\mathrm{H}}/h) = 1.1 \cdot 10^6 \text{ sec}^{-1} \quad \text{and} \quad (A_{\mathrm{D}}/h) = 1.5 \cdot 10^5 \text{ sec}^{-1}.$$

* Measurements were performed by N. F. Usacheva.

According to the theory developed by Ramsey (^{8}), $(A/h) \sim \gamma|\psi(0)|^2$; here γ is the gyromagnetic factor of the nucleus and $|\psi(0)|^2$ is the probability density for finding the unpaired electron at the nucleus. Taking this relation into account, we can write:

$$\frac{\gamma_H |\psi(0)_H|^2}{\gamma_D |\psi(0)_D|^2} = \frac{(A_H/h)}{(A_D/h)} = 7.3. \tag{6}$$

Since $(\gamma_H/\gamma_D) = 6.53$, it follows from (6) that $|\psi(0)_D|^2 = 0.9|\psi(0)_H|^2$. Thus, the density of the unpaired electrons of the Mn^{2+} ion at the positions of the deuterons is somewhat smaller than at the positions of the protons. This statement is consistent with the known fact that cations are less strongly hydrated in heavy water than in light water (^{9}).

It may be assumed that, in the temperature range studied, the constant A does not depend on temperature (^{1,2}). Then, using the quantities (A_H/h) and (A_D/h) determined above, from the curves of Fig. 2, with the aid of (4), we find the temperature dependences of $\tau_{\varepsilon\mathrm{H}}$ and $\tau_{\varepsilon\mathrm{D}}$. Since the temperature dependence τ_s is known (^{7}), the desired quantities τ_H and τ_D are readily determined from equation (5): $\tau_H(300°\mathrm{K}) = 1.6 \cdot 10^{-8}$ sec and $\tau_D(300°\mathrm{K}) = 1.4 \cdot 10^{-8}$ sec.

Fig. 2. Temperature dependence of the exchange contributions to the NMR times of protons (a) and deuterons (b) in a solution of Mn^{2+} ions in a mixture of 50% H_2O + 50% D_2O, calculated from the measurement results

Figure 1: Fig. 2. Temperature dependence of the exchange contributions to the NMR times of protons (a) and deuterons (b) in a solution of Mn^{2+} ions in a mixture of 50% H_2O + 50% D_2O, calculated from the measurement results

Fig. 2. Temperature dependence of the exchange contributions to the NMR times of protons (*a*) and deuterons (*b*) in a solution of Mn^{2+} ions in a mixture of 50% H_2O + 50% D_2O, calculated from the measurement results.

The temperature dependence of these times is described by the exponents $\tau_H = \tau_H^0 \exp(V_H/RT)$ and $\tau_D = \tau_D^0 \exp(V_D/RT)$, with activation energies

$$V_H = 8.3 \text{ kcal/mol} \quad \text{and} \quad V_D = 8.0 \text{ kcal/mol}.$$

The obtained values of the activation energies indicate that it is not proton chemical exchange, but exchange by water molecules, that averages the $A \cdot I \cdot S$ interaction in aqueous solutions of Mn^{2+} ions. In favor of this is the small difference between the values of V_H and V_D found by us, whereas isotope-exchange experiments have established ([10]) that the activation energy of deuteron exchange is greater than that for proton exchange, and that for the hydroxyl bond $V_D - V_H \approx 1.4$ kcal/mol. Such a difference arises mainly from the difference between the zero-point vibrational energies of the O—H and O—D bonds and gives $\tau_D/\tau_H \sim 10$ ([10]).

According to ([11]), the activation energy of proton exchange in the O—H bond cannot be less than the energy interval between the ground and first excited vibrational levels of this bond. The shifts of the vibrational frequencies of the O—H bonds of molecules entering the first hydration shell of cations amount to 5-10% of the O—H bond frequency in the pure solvent ([12,13]). Hence the minimum value is $V_H \cong 10$ kcal/mol. Such a value of the activation energy of proton exchange was obtained in work ([2]) in an aqueous solution of Cr^{3+} ions; moreover, it was established that exchange by water molecules around the cation proceeds very slowly.

The height of the barrier for molecular water exchange around the Mn^{2+} ion, calculated by the formula given in ([14]), proves to be equal to

8.8 kcal/mol, which agrees with the experimental data obtained by us*.

The established rapid exchange of water molecules between the first hydration shell of the Mn^{2+} ion and the remaining mass of the solvent agrees with the concept of hydration developed by O. Ya. Samoilov ([16,17]).

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* The ion-radius values required for this calculation were taken from work ([15]).

Note: Figure translations are in progress. See original paper for figures.

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