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Abstract

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PROTON RELAXATION IN H_2O-D_2O MIXTURES CONTAINING PARAMAGNETIC IONS

(Presented by Academician M. A. Leontovich, 5 X 1956)

In order to further study the mechanism of the spin-lattice relaxation constant in solutions of paramagnetic salts (^{1}), we have carried out measurements of the longitudinal relaxation time of protons T_1 in solutions in which the content of relaxing nuclei H^1 was varied over wide limits by partial replacement of ordinary (light) water H_2O by heavy water D_2O.

The results obtained for solutions of $MnCl_2$, 0.003 mole/liter, $Cr(NO_3)_3$, 0.005 mole/liter, $Cu(NO_3)_2$, 0.03 mole/liter, and $CoSO_4$, 0.25 mole/liter, are presented in Fig. 1. As follows from the curves, as the proton concentration decreases, a very strong lengthening of the time T_0 occurs. When 90% of the total number of protons in the solutions are replaced by deuterons ($\alpha = 0.9$), T_1 increases by more than an order of magnitude.

The observed effect is somewhat unexpected: it would seem that the relaxation time of protons should not depend on the isotopic composition of the solvent (water). It is well known that the time T_1 in paramagnetic solutions is determined by the fluctuating dipole magnetic interaction between paramagnetic ions and protons of the solvent (^{2}) (the magnetic interaction between the nuclei themselves is small and does not make a noticeable contribution to T_1). But when H_2O molecules are replaced by D_2O, neither the structure of the solutions nor the local magnetic fields created by the ions are substantially changed. Moreover, numerous measurements in aqueous solutions have shown (^{2,4}) that even a very large decrease in the concentration of paramagnetic ions N does not cause anomalies in the relaxation process: the product $T_1 N$ remains practically constant, in agreement with the requirements of theory (^{2}).

Taking the above into account, it seems to us that the only possible explanation of the experiment is the following: equalization of the spin temperature of the protons T_s (^{5}) in the immediate environment of paramagnetic ions* takes place not through Brownian motion of water molecules, but as a result of molecular transfer (exchange) of hydrogen ions. Neighboring water molecules exchange protons through continuously forming and breaking hydrogen bonds (^{6}). The introduction of heavy water into the solutions, owing to its lower chemical re-

Fig. 1

Figure 1: Fig. 1

activity in comparison with ordinary water (7), slows the proton exchange**, which leads to the observed increase in the time T_1.

We have already noted the influence of short-range order on the effect of proton relaxation in paramagnetic solutions (1). Evidently, the stability of the hydration atmosphere in the immediate environment of paramagnetic ions is so high that simple thermal transfer of water molecules here does not provide sufficient equalization of the spin temperature T_s during a time $\ll T_1$ ($10^{-2} \div 10^{-4}$ sec).

* What is meant is the process of establishing thermodynamic equilibrium within the nuclear spin system.

** This can be shown on the basis of the theory of protolytic reactions (7).

An approximate calculation shows that the absence of effective Brownian translation in the first two or three layers of water molecules adjacent to the ions is sufficient to explain the observed phenomenon.

From Fig. 1 it is seen that each of the four investigated solutions gives its own, distinct course of the curve. The indicated difference does not lie within the limits of experimental error. In the case of solutions of divalent ions Co^{2+} ($N = 0.25$ mole/l), Cu^{2+} ($N = 0.03$ mole/l), and Mn^{2+} ($N = 0.003$ mole/l), it can be qualitatively explained by the difference in the concentrations N used: with a larger

Fig. 1. Ratio of the longitudinal proton relaxation time T_1 for a solution in ordinary water to the time T_1 for the same solution containing heavy water, as a function of the relative volume content of heavy water in the solutions: 1 – $MnCl_2$, 0.003 mole/l; 2 – $Cr(NO_3)_3$, 0.005 mole/l; 3 – $Cu(NO_3)_2$, 0.03 mole/l; 4 – $CoSO_4$, 0.25 mole/l.

number of paramagnetic ions in the solution, proton exchange should play a smaller role, since the relative number of protons directly interacting with the paramagnetic ions increases. As for the chromium solution, the stronger dependence of T_1 on α found for it, compared with the manganese solution of similar concentration, may indicate a somewhat greater height of the hydrate atmosphere surrounding the trivalent Cr^{3+} ions.

The results presented above were obtained at room temperature and in a constant magnetic field $H_0 \sim 230$ Oe. The measurement method was the same as in work (1). Since the measurements were carried out with samples containing unequal numbers of protons, a series of control experiments was performed which proved the strict linearity of the apparatus: the intensity of the resonance signal decreased linearly with a decrease in the number of protons in the samples, provided that the relaxation time T_1 and the filling factor of the measuring coil remained unchanged.

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