Spin-Lattice Relaxation Times of ^{1}H in Aqueous Gadolinium Chloride Solutions

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Spin-lattice relaxation times T_1 of protons in aqueous solutions of gadolinium chloride have been measured at 2.11 T for a larger range of concentrations down to 0.035 millimolal. Very small amounts of $GdCl_3$ decrease strongly T_1 of the water protons.

In NMR-imaging, the signal intensity depends strongly on the relaxation times T_1, T_2 and the pulse shape and sequence of the excitation frequency (see e.g. [1]). Varying these parameters the image contrast can be changed. The relaxation times are impacted by paramagnetic species, and it has been well known since the early days of NMR spectroscopy that paramagnetic ions of transition elements and rare earths change e.g. the relaxation times of protons in water very typically (2–8). Relatively few data are available for T_1 of protons in aqueous solutions of rare earth ions [5, 9–13], especially at low concentrations.

In the following we report on measurements of T_1 of protons in aqueous solutions of $GdCl_3$ for a wide range of concentrations, as well as on T_2 for higher concentrations.

The T_1 measurements of ^{1}H were performed at 90 MHz by the Fourier transform inversion recovery method [14–16] using a Bruker pulse spectrometer SXP 4-100, an externally NMR-stabilized Bruker magnet system working at 2.11 T and a B-NC12 data unit. The samples have been prepared by weighing salt and water of high purity. They are not degassed for having realistic conditions. The temperature was (299 ± 1) K.

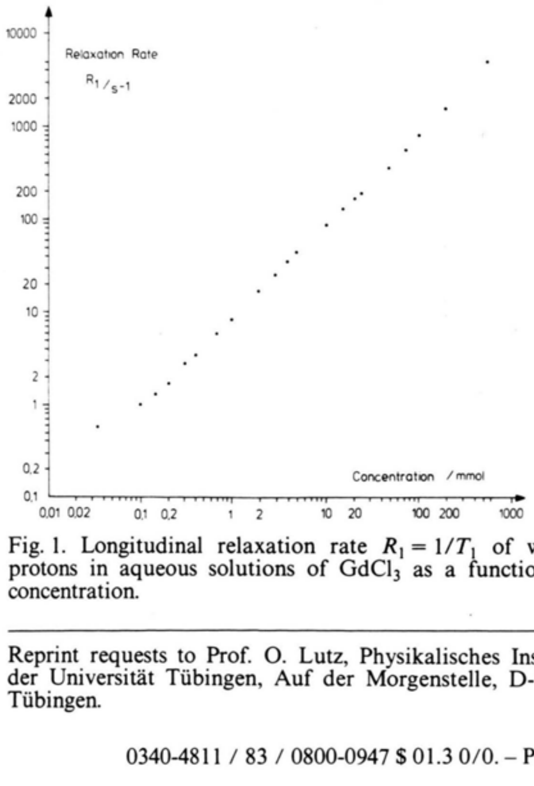

Fig. 1. Longitudinal relaxation rate $R_1 = 1/T_1$ of water protons in aqueous solutions of $GdCl_3$ as a function of concentration.

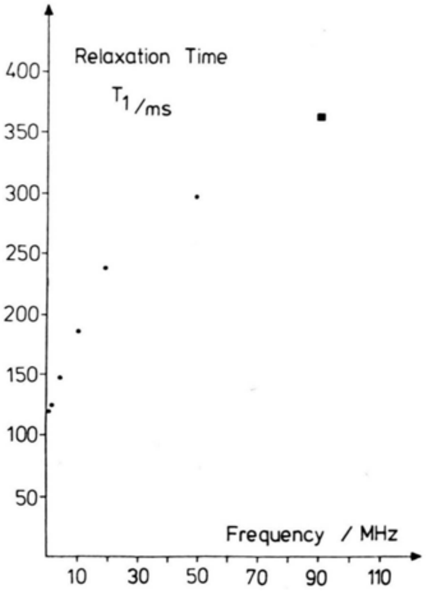

Fig. 2. Longitudinal relaxation times T_1 of water protons in a 0.3 millimolal aqueous solution of $GdCl_3$ at 25 °C as a function of the Larmor frequency. Value at 90 MHz (■) this work, the other data (●) are taken from the work of König and Epstein (11).

In Fig. 1 the results for the relaxation rates $R_1 = 1/T_1$ are presented in double logarithmic scale since the concentration ranges from 0.035 millimolal to 500 millimolal and the relaxation rate from 0.5 s^{-1} to 500 s^{-1}. For the convenience of the reader, in Table 1 the data for the smaller concentrations are given. It is obvious that very small concentrations shorten the relaxation time strongly: in the 0.035 millimolal Gd^{3+} solution T_1 is reduced to 1.7 s. T_1 varies nearly linearly with the concentration of Gd^{3+}. Some data for T_1 have been measured in solutions of $MnCl_2$. The Mn^{2+} ion is about 5% to 15% less effective on T_1, depending on concentration. A further interesting fact in aqueous solutions of paramagnetic ions was also established: T_1 and T_2 differ significantly depending on the sort of ion [5, 8]. In the case of Gd^{3+} at the mentioned field and for concentrations of 20 millimolal to 500 millimolal, T_2 is about a factor of 1.9 to 1.6 shorter than T_1.

Further, the longitudinal relaxation times of ^{1}H in paramagnetic aqueous solutions depend on the strength of the magnetic field that means change with the Larmor frequency [6]. König and Epstein [11] have given T_1 data for a 0.3 millimolal aqueous solution of $GdCl_3$ up to 50 MHz, e.g. at 25 °C. Between 2 MHz and 20 MHz a change by about a factor of 2 is reported. Some of their data together with the comparable value measured at 90 MHz in this work are given in Figure 2. The knowledge of this field

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Concentrations (millimolal)	T_1 (ms)
0	3030
0.035	1745
0.1	1010
0.14	750
0.2	575
0.3	360
0.4	291
0.7	174
1.0	122
2.0	60
3.0	40
4.0	29
5.0	23
10.0	12.0
15.0	8.0
21.0	6.0

Table 1. Longitudinal relaxation time T_1 of ^{1}H in solutions of $GdCl_3$ in H_2O. The errors are less than 5%.

dependence is very important for applications in NMR imaging. From the figure one derives that in fields which are used in NMR imaging, the longitudinal relaxation times are about a factor of two shorter than in the high field. That means, that the proton relaxation time in a 0.02 millimolal aqueous solution of $GdCl_3$ is expected to be about half of that in pure water. Consequently, the signal intensities can be impacted by very low concentrations. Recently, an observation of such an effect using Mn^{2+} ions was reported for an *in vivo* system [17].

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