# Nuclear magnetic relaxation in acqueous solutions of strong acids

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We have measured the proton spin-lattice relaxation time $T_1$ [1] in oxygen-free solutions of nitric acid and hydrochloric acid at different concentrations. Such solutions have already been studied by several authors [2-4] by means of measurements of chemical shift. All these authors agree on the occurence in these solutions of fast proton transfer between molecular groups. We must therefore expect to observe a unique proton spin-lattice relaxation time [5, 6]. Actually the return of the longitudinal component of the nuclear magnetization to the equilibrium
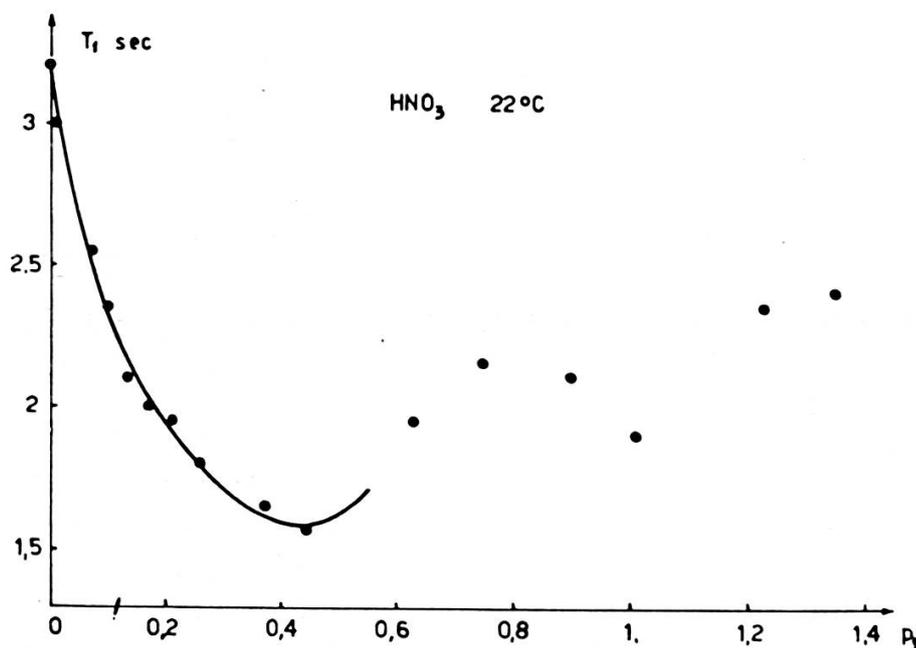


Fig. 1.

$T_1$ of acqueous solutions of nitric acid versus the proton concentration $p_1$ in the $H_3O^+$ group. This quantity is related to the molar fraction of acid $N_1$ by the relationship $p_1 = 3N_1/(2 - N_1)$.

value, which we have studied with a technique previously described [7], has always been found exponential within the limits of resolution of our experimental apparatus.

The experimental results we obtained for $HNO_3$ are shown in figure 1.

We tried to interpret these results, at least qualitatively, making the following assumptions: *(a)* the acid is completely dissociated; *(b)* the reciprocal of the proton relaxation time we measure is the weighted average of the reciprocals of the relaxation times of the protons in the water molecules and in the hydronium ions

$$\frac{1}{T_1} = \frac{p_1}{(T_1)_{H_3O^+}} + \frac{1 - p_1}{(T_1)_{H_2O}} ;$$
(1)

*(c)* the relaxation times $(T_1)_{H_3O^+}$ and $(T_1)_{H_2O}$ are related to the viscosity $\eta$ of the solution according to the theory of B.P.P. [8].

$$\frac{1}{(T_1)_{H_3O^+}} = \left(\frac{1}{T_1}\right)_{intra} + \left(\frac{1}{T_1}\right)_{inter} = A_{H_3O^+}\, \eta + B\, \eta\, N$$

$$\frac{1}{(T_1)_{H_2O}} = \left(\frac{1}{T_1}\right)_{intra} + \left(\frac{1}{T_1}\right)_{inter} = A_{H_2O}\, \eta + B\, \eta\, N$$
(2)

where $N$ is the number of protons per cm$^3$, $A_{H_3O^+}$ and $A_{H_2O}$ are characteristic constants and $B$ is a constant which we assume to be approximatively equal for the two groups; in fact it seems reasonable to assume to be unimportant for the intermolecular interactions which group carries the protons, provided that the proton-carrying molecules have about the same size.

From the equations (1) and (2) we obtain for the measured relaxation time:

$$\frac{1}{T_1} = A_{H_3O^+}\, \eta\, p_1 + A_{H_2O}\, \eta\, (1 - p_1) + B\, \eta\, N$$
(3)

from which we have

$$\frac{1}{T_1 \eta} - BN = p_1 A_{H_3O^+} + (1 - p_1) A_{H_2O} .$$
(4)

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In figure 2 are plotted the experimental quantities $1/T_1\eta$ and the difference $1/T_1\eta - BN$ versus $p_1$. We assumed for $B$ the value that can be calculated with the help of the theory of B.P.P.
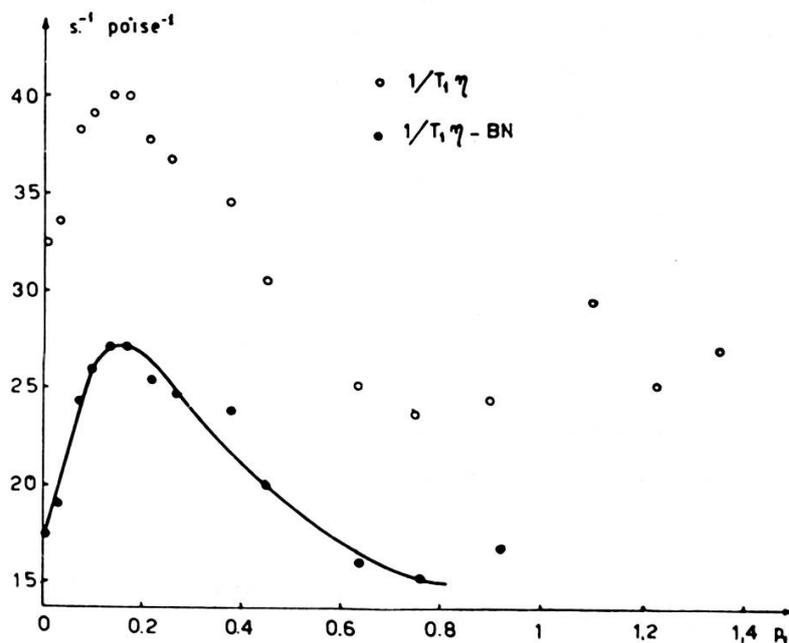


Fig. 2.

$1/T_1\eta$ and the difference $1/T_1\eta - BN$ versus $p_1$ for acqueous solutions of nitric acid.

It can be seen in figure 2 that the difference $1/T_1\eta - BN$ depends linearly on $p_1$, as required by the equation (3), only for concentrations up to 6 moles per liter.

The slope of the experimental curve for low concentrations of acid allows us, in principle, to evaluate $A$ for the hydronium ion. The value of about $90\ \text{sec}^{-1}\ \text{poise}^{-1}$, thereby obtained, may be compared with the value of $66\ \text{sec}^{-1}\ \text{poise}^{-1}$ which we have obtained using the model suggested by Hubbard for a three-spin system [10]. In these calculations we assumed as interproton distance for the hydronium ion the value $b = 1.65\ \mathring{A}$, given in ref. 11, and as molecular radius the value $a = 1.9\ \mathring{A}$, suggested in ref. 9.

The deviation from a straight line of the curve of figure 2 at higher concentrations may be accounted for whith the presence of undissociated acid molecules. If we introduce an apparent degree of dissociation $\alpha < 1$ and we take into account the contribution of the undissociated nitric acid molecules to the measured relaxation time, we obtain

$$\frac{1}{T_1 \eta} - BN = p_1 A_{H_3 O^+} + (1 - p_1) A_{H_2 O} - \frac{(1 - \alpha)}{3} (3 A_{H_3 O^+} -$$

$$2 A_{H_2 O} - A_{HN O_3}) . \qquad (5)$$

As the quantity $A_{HN O_3}$ is negligible, for the presence of only one proton in the nitric acid molecule, the term in parenthesis is certainly positive.

It is therefore evident that the introduction of a degree of dissociation $\alpha < 1$ decreasing with the increasing of concentration accounts qualitatively for the increasing deviation of the experimental curve from a straight line. The value of $\alpha$ we must introduce in the equation (4) in order to obtain a quantitative agreement with our experimental results are however considerably lower than the values obtained from Raman spectroscopy [12] and from measurements of chemical shift [3].

For a concentration of about $p_1 = 0.7$ the experimental curve reaches a minimum; for $p_1 > 0.7$ the experimental points do not seem to stay on a smooth curve. This minimum and the following irregularities might be attributed to hydratation and polymerization of the acid. On the other hand at high acid concentrations the measurements were difficult to perform because of the few protons present in the solutions.

Measurements of $T_1$ for two solutions of $HNO_3$ at various temperatures have been also performed. The experimental results, which are given in figure 3, show that the quantity $T/T_1\eta$ is not constant with the varying of temperature, as we should expect, but increases slightly with the increasing
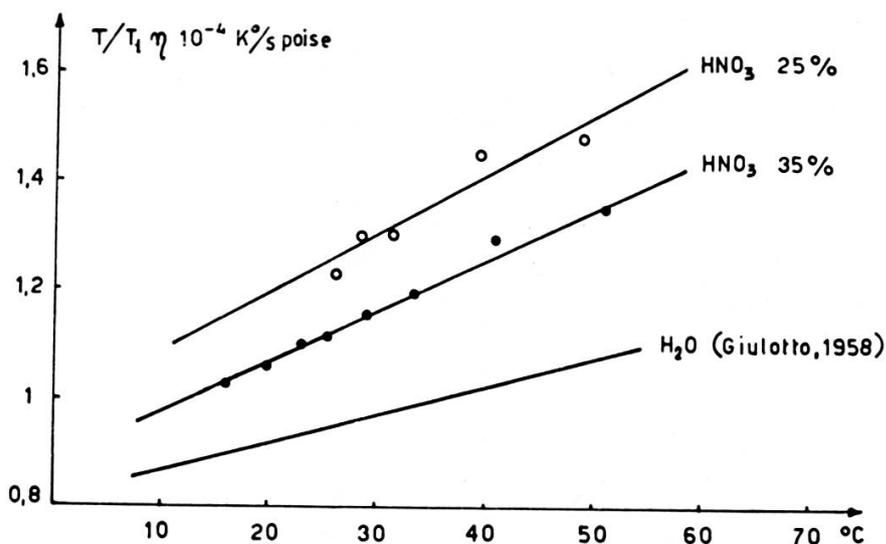


Fig. 3.

$T/T_1\eta$ versus $T$ for two samples of acqueous solutions of nitric acid.

of temperature. It may be pointed out that the same behaviour of $T/T_1\eta$ with the varying of temperature has been observed for water [13].
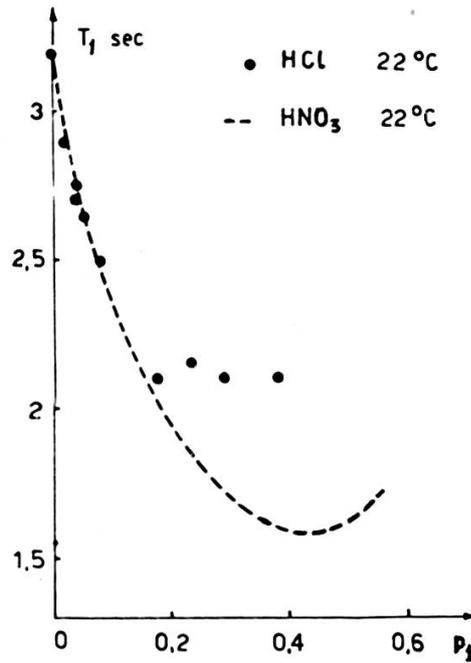


Fig. 4.

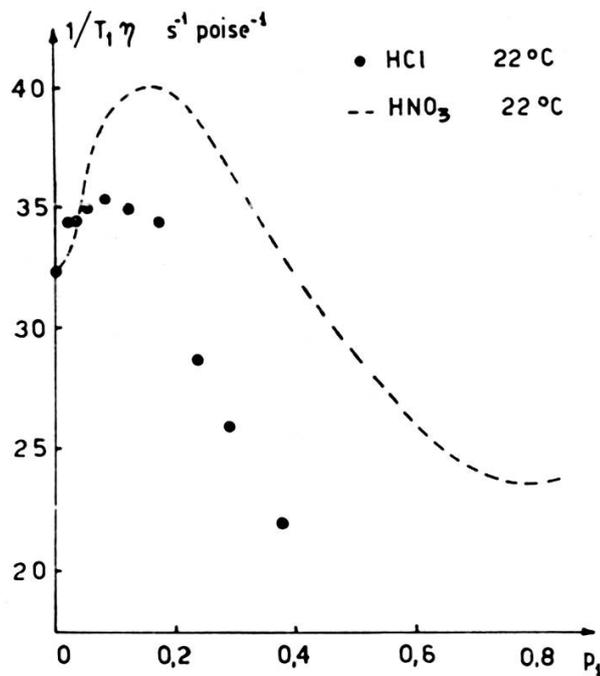$T_1$ versus $p_1$ for acqueous solutions of hydrocloric acid. The dashed curve is that of figure 1.



Fig. 5.

$1/T_1\eta$ versus $p_1$ for aqueous solutions of hydrocloric acid. The dashed curve is the corresponding curve for $HNO_3$.

Measurements on acqueous solutions of hydrochloric acid have been also performed. In figures 4 and 5 the relaxation time $T_1$ and the quantity $1/T_1\eta$ for solutions of $HCl$ are plotted versus $p_1$.

It is possible to make for $HCl$ the same assumptions that were made for $HNO_3$; therefore we should expect that the plot of $1/T_1\eta$ versus $p_1$ should be about the same for the two acids, at least at low concentrations of acid. It is seen in figure 4 that the plot of $1/T_1\eta$ versus $p_1$ for $HCl$ is rather different from the corresponding curve for $HNO_3$. It does not seem possible to explain this behaviour in a simple manner.

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