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## Proton Relaxation and Hydration in Aqueous Solutions of $\text{Mn}^{++}$ Ions

par H. PFEIFER

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We have measured the temperature dependence of the proton  $T_1$  and  $T_2$  in an aqueous solution containing  $3 \times 10^{18}$   $\text{Mn}^{++}$  ions/cm<sup>3</sup> at 4 and 16 Mc/sec (cp. [1]). At these frequencies the contribution of the exchange interaction to  $T_1$  is negligible [2], so that the equations for  $T_1$  contain only two unknown quantities, namely  $m/b^6$  and  $\tau$ .  $m$  is the number of the next neighbouring water molecules (first hydration sphere) of a  $\text{Mn}^{++}$  ion,  $b$  the distance between the  $\text{Mn}^{++}$  ion and the protons of these water molecules, and  $\tau$  the correlation time for the fluctuating rotation of the  $\text{Mn}^{++}$  ion with its next neighbouring water molecules. We denote by  $b_0$  the value of  $b$ , which follows from a geometrical point of view for the case that one assumes that the electrical dipoles of the water molecules are oriented in a radial direction, and that the radius of the  $\text{Mn}^{++}$  ion is equal to the value given by Goldschmidt [3]. The radius of the water molecule was taken from the results of X-ray diffraction at 0° C [4]. Then follows from the temperature dependence of  $T_1$  at 4 and 16 Mc/sec that the quantity  $m (b_0/b)^6$  decreases from 15.5 for 0° C down to 5.6 for 100° C with a maximal error smaller than 10%. Because of the fact, that the number  $m$  of the next neighbouring water molecules must lie between 8 and 3 (the upper value results from the ratio of the radii and the lower from the coordination number of water and the fact that  $\text{Mn}^{++}$  shows positive hydration [4]) this result corresponds to a constant  $b = 0.9 b_0$  (if  $m$  decreases from 8 to 3), to an increase of  $b$  by the factor 1.19 (if  $m$  is constant) or to an increase of  $b$  by the factor 1.4 (if  $m$  increases from 3 to 8). The increase of the effective radius of the water molecule measured by X-ray diffraction [5] only corresponds to an increase by a factor 1.06, so that our results may be explained by a strong decrease of  $m$ , or more probably by a nonradial direction of the water molecules, which become more and more radial oriented with increasing temperature. The last explanation is supported by the fact that in all cases  $b$  is smaller than  $b_0$  for temperatures smaller than about 40° C.

The second quantity, the temperature dependence of which could be investigated, was  $\tau$ , the correlation time for the fluctuating rotation of the  $\text{Mn}^{++}$  ion with its next neighbouring water molecules. This quantity follows from a solution of the ordinary diffusion equation [6]. In the case of a sphere with a radius large compared with the radius of the water molecules, the diffusion constant is related to the temperature, to the viscosity and to the radius of the sphere by the well known equation of Stokes. With the measured correlation time for the  $\text{Mn}^{++}$  ion with its next neighbouring water molecules one can calculate by this equation an effective of Stokes radius, the ratio of which to the «real radius» is a measure of the influence of the structure of water. Of course the «real radius» is unknown, and we take instead of it the sum  $a_0$  of the  $\text{Mn}^{++}$  radius after Goldschmidt [3] and the diameter of the water molecule calculated from the X-ray diffraction at  $0^\circ\text{C}$  [4]. Then one finds from the temperature dependence of  $T_1$  at 4 and 16 Mc/sec, that the ratio  $a/a_0$  increases from 0.65 for  $0^\circ\text{C}$  to 0.95 for  $100^\circ\text{C}$  with a maximal error smaller than 5%. This strong increase of  $a/a_0$  cannot only be explained by an increase of the mean radius of the water molecules, but refers to the fact, that the water becomes a more homogeneous liquid (decreasing ice structure) with increasing temperature [4].

The measurements of  $T_2$  give the temperature dependence of the quantity  $m (A/h)^2 \tau_x$  at 4 and 16 Mc/sec.  $A/h$  is the coupling constant of the exchange interaction and  $\tau_x$  the corresponding correlation time, which is equal either to the paramagnetic relaxation time of the  $\text{Mn}^{++}$  ion or to the mean lifetime of the protons in the hydration sphere. The results show that the ratio of  $(A/h) \sqrt{\tau_x}$  at 16 Mc/sec and 4 Mc/sec is not independent of the temperature and equal to 1.72 for  $0^\circ\text{C}$  and 1 for  $100^\circ\text{C}$ . The quantity  $m (A/h)^2 \tau_x$  itself at 4 Mc/sec shows a maximum near  $50^\circ\text{C}$  with such a strong increase from low temperatures, that it may not only be explained by the increase of the paramagnetic  $\text{Mn}^{++}$  relaxation time [7, 8].

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