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Proton Relaxation Times in H_2O-D_2O Mixtures

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The relaxation time, T_1, of protons in H_2O-D_2O mixtures has been measured and found to depend strongly upon the relative proton concentration. This dependence supports the assumption of Bloembergen, Purcell, and Pound that the main relaxation mechanism in water is a nuclear dipole interaction.

THE relaxation of protons in water has been assumed in the theory of Bloembergen, Purcell, and Pound[1] to be due predominantly to their mutual dipole interaction. As a severe test of this assumption, measurements of the longitudinal relaxation time T_1 of protons in mixtures of light and heavy water have been carried out. Due to its smaller magnetic moment, which enters quadratically in the relaxation process, a deuteron should be about ten times less effective for the relaxation of neighboring protons than another proton. A corresponding lengthening of T_1 in mixtures with increasing concentration of heavy water would thus represent a verification of the above-mentioned assumption.

Measurements of T_1 in H_2O-D_2O mixtures were carried out with a nuclear induction apparatus in a magnetic field of about 7000 gauss by using the method of total reversal of the proton polarization.[2] The nuclei were allowed to establish their equilibrium polarization whereupon the proton polarization was completely reversed by sweeping the field through resonance. The resonance was traversed during a time Δt which satisfied, to within a factor of at least ten, the condition

$$1/(\gamma H_1) \ll \Delta t \ll T_1, \tag{1}$$

where γ is the proton gyromagnetic ratio and $2H_1$ the amplitude of the transverse radio-frequency field.

The proton polarization after reversal recovers its equilibrium value with the characteristic time T_1 and is zero at a time $(\ln 2)\, T_1$ after the reversal. For equal short intervals on either side of this time, the observed proton signal is symmetrically inverted, allowing the accurate determination of the time of zero polarization, as a convenient experimental measure of T_1. The shorter range of times for which the signal was so small as not to be detectable above the noise has been taken as a measure of the experimental error in the method.

The first samples examined were prepared by sealing the mixtures in Pyrex tubes; however, we were led to suspect that in these samples significant amounts of paramagnetic material, perhaps iron salts, were being dissolved slowly from the walls. The samples were subsequently prepared by direct vacuum distillation into quartz tubes. These were carefully sealed against air since oxygen dissolves in water in quantities sufficient to contribute appreciably to the relaxation of the protons.[3]

Figure 1 represents the experimental data for $1/T_1$ of H_2O-D_2O mixtures as a function of the volume concentration, α, of ordinary water in heavy water. The data show indeed the strong dependence of T_1 on α which is to be expected from a relaxation process based on a mutual dipole interaction among the nuclei.

According to the theory of Bloembergen *et al.*, which assumes that the correlation times are proportional to the macroscopic viscosity, the relaxation time of the mixture should obey an expression of the form

$$\frac{1}{T_1} = \eta \left(\frac{1}{T_1}\right)_w [\alpha + (1-\alpha)R], \tag{2}$$

where the index w refers to ordinary water and η is the

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[1] Bloembergen, Purcell, and Pound, Phys. Rev. 73, 679 (1948).

[2] Chiarotti, Cristiani, Giulotto, and Lanzi, Nuovo cimento 12, 519 (1954).

[3] Chiarotti, Christiani, and Giulotto, Nuovo cimento 1, 863 (1955).

ratio of the viscosity of the mixture to that of ordinary water. The quantity R is given by

$$R=\frac{\mu_d^2}{\mu_p^2}\frac{I_d+1}{I_d}\frac{I_p}{I_p+1}=0.063, \qquad (3)$$

where μ_p, μ_d are the magnetic moments and I_p, I_d the spins of the protons and deuterons respectively.[4]

It will be noted from (2) that $1/(\eta T_1)$ should be a linear function of α. We have plotted this quantity, using the observed values[5] of η, in Fig. 2. The points lie on a straight line to within the experimental error, showing that the assumption of proportionality between the correlation time and the macroscopic viscosity is substantially correct.

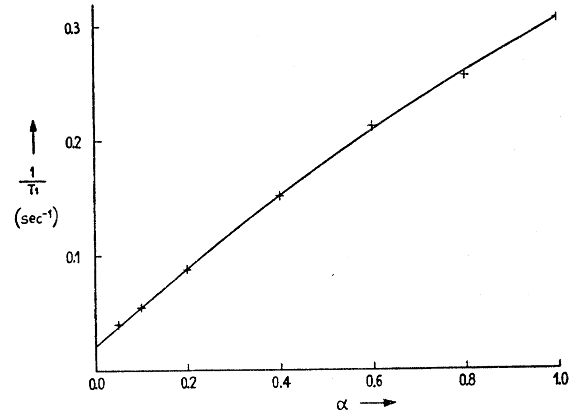

FIG. 1. Reciprocal of measured proton relaxation time, T_1, *vs* relative volume concentration, α, of ordinary water in H_2O-D_2O mixtures. The temperature was 21.5°C. The variation of the temperature of the various samples was 0.6°C or less; however, a slight correction has been made for this variation.

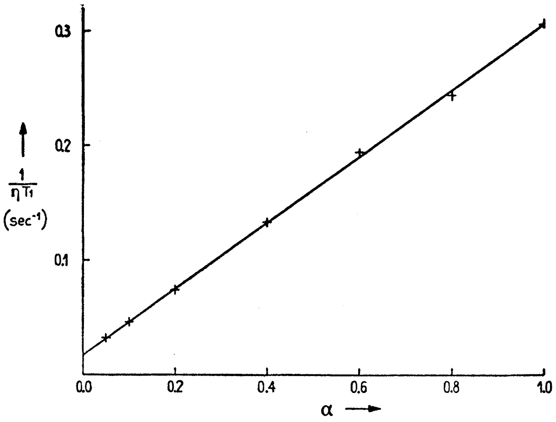

FIG. 2. Reciprocal of the product of the proton relaxation time, T_1, and the relative viscosity, η, *vs* relative volume concentration, α, of ordinary water in H_2O-D_2O mixtures.

From the plot of Fig. 2, the experimental value of R is found to be

$$R_{\text{exp}}=0.056\pm0.010. \qquad (4)$$

In view of the somewhat uncertain assumption, the close agreement of the values (3) and (4) must be considered as rather fortuitous. However, it is not the exact numerical value of R but the fact that it is small in comparison to unity which leads to the strong dependence of T_1 on α and thus to the verification of magnetic dipole relaxation in water.

ACKNOWLEDGMENTS

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[4] Professor A. Abragam has kindly pointed out in a private communication that the coefficient R should be multiplied by a factor $\frac{4}{3}$. However, the inclusion of this factor would not materially affect our conclusions since the observed effects depend primarily upon the smallness of R compared to unity.

[5] W. N. Baker and V. K. LaMer, J. Chem. Phys. **3**, 406 (1935); G. N. Lewis and R. T. MacDonald, J. Am. Chem. Soc. **55**, 4730 (1933); R. C. Hardy and R. L. Cottingham, J. Chem. Phys. **17**, 509 (1949).