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Proton magnetic resonance relaxation and self diffusion in the primary alcohols at 25° C.

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Résumé.

On a mesuré les temps de relaxation T_1 pour un champ polarisant de 250 gauss et T_2 pour un champ de 0,73 gauss et le coefficient de diffusion (Δ) pour l'eau et les alcools de CH_3OH à $\text{C}_8\text{H}_{17}\text{OH}$ à 25° C. Il y a une relation très nette entre T_2 et Δ pour toute la série: T_2/Δ est constant. Ceci indique, puisque T_2 dépend, en gros, du déplacement des chaînons, que Δ en dépend principalement aussi. Donc T_2 n'est pas relié au déplacement du dipôle ($-\text{OH}$) et l'on explique ainsi l'absence d'une relation simple entre T_2 et ν (diélectr.) dans ces composés. On note aussi un comportement compliqué de T_1 pour l'alcool méthylique et une différence entre T_1 et T_2 pour l'alcool méthylique et pour l'eau.

We have measured the proton magnetic resonance relaxation times T_1 and T_2 and the self diffusion constant Δ for a number of primary alcohols and water at 25° C. The method used was a synthesis of the free precession [1] and the echo techniques [2, 3] which has been described elsewhere [4]. The polarising field was 250 ± 25 gauss and so the T_1 values refer to this field. There is no great experimental difficulty in measuring long T_1 values, even much longer than the few seconds reported here, and we shall not dwell on this. Measurement of T_2 , which we have performed in the earth's field slightly augmented by external coils (0.73 gauss or 3.1 kc/s for protons), is very difficult where T_2 is several seconds or longer because of diverse effects which nearly all tend to make T_2 appear shorter. We have been to considerable pains to remove these effects as already described [4] and we believe that the T_2 values reported here are as accurate as the T_1 values. This is of some importance in water and methyl alcohol.

T_1 is determined by measuring the magnitude of the nuclear polarisation (M_z) produced during a time t , by producing an echo at constant delay. If M_z varies exponentially with time $M_z = M_0 (1 - \exp - t/T_1)$ which defines

T_1 and we plot $\ln [1 - A(t)/A(\infty)]$ versus t , where $A(t)$ is the echo amplitude for a polarisation time t . The slope of the line gives T_1 as in Figure 1 for ethyl alcohol at 25° C. In all cases reported here a straight line was obtained except for methyl alcohol as shown in Figure 2. This curve does not fit a decay of the form $M_z = \frac{3}{4} M_0 (1 - \exp -t/T_{\text{ICH}_3}) + \frac{1}{4} M_0 (1 - \exp -t/T_{\text{OH}})$ as might perhaps have been expected for methyl alcohol (CH_3OH),

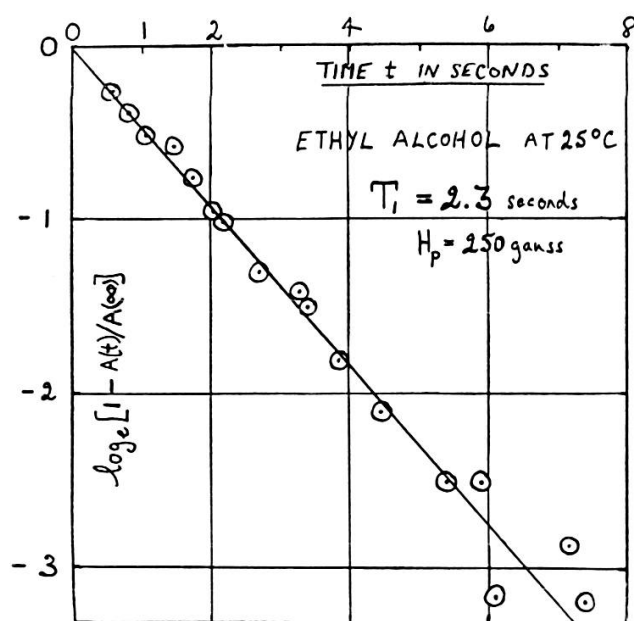


Fig. 1.

or indeed any sum of exponential decays. The decay curve would have been expected to resolve in this simple way if the two signals are independent because the chemical shift of the methyl and hydroxyl protons at 250 gauss is 2.4 c/s and this is much larger than the true line width $1/2\pi T_2 \simeq 0.064$ c/s. A recent theory [5] suggests that there should be multiple T_1 relaxation when nuclei of spin $1/2$ interact in groups of three or more. However the relative intensities for a CH_3 group as in methyl alcohol predicted by Hubbard are not readily observed and cannot explain the curve in Figure 2. An explanation in terms of Perrin's [6] theory of multiple correlation times for the reorientation of ellipsoidal molecules is a possibility [7]. A previously reported values of T_1 in methyl alcohol is 8 seconds at 20° C and $H_0 = 1650$ gauss [8].

T_2 was measured from the variation of echo amplitude $\mathcal{A}(2\tau)$ at 2τ due to a 180° pulse applied τ after cutting the polarising field which had been

maintained for much longer than T_1 . In all cases, including methyl alcohol, the decay of transverse magnetisation was exponential, i.e. a single T_2 . In the presence of self diffusion effects, in the inhomogeneity of the main field, the echo amplitude for a single 180° pulse is given by

$$\alpha(2\tau)/\alpha(0) = \exp \left[- (2\tau)/T_2 - (2\tau)^3/T_D^3 \right]$$

where

$$T_D^3 = 12/\Delta\gamma^2 G^2$$

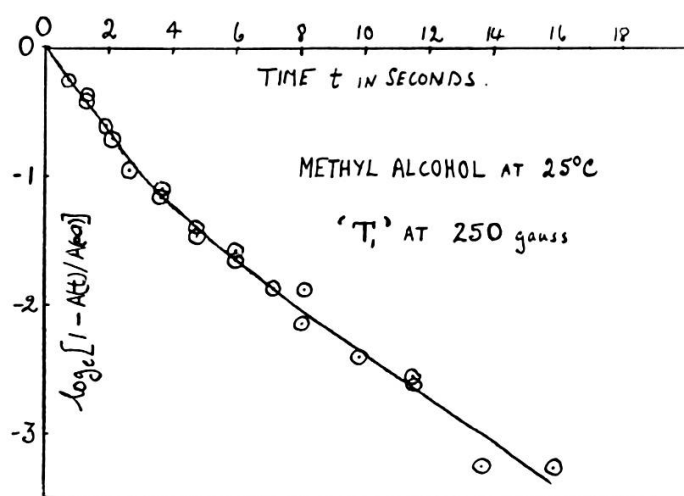


Fig. 2.

and Δ is the self diffusion constant and G is the linear field gradient. Hence $\frac{1}{(2\tau)} \ln \alpha(2\tau)/\alpha(0) = -1/T_2 - (1/T_D^3)(2\tau)^2$ and a plot of $\frac{1}{(2\tau)} \ln \alpha(2\tau)/\alpha(0)$ against $(2\tau)^2$ should be a straight line of slope $(-1/T_D^3)$ and intercept $-1/T_2$. Figure 3 shows this curve for ethyl alcohol. When T_D is comparable in magnitude with T_2 this is a satisfactory way of measuring both T_2 and T_D .

The results for the normal alcohols and water are shown in columns (1), (2) and (3) of the Table. A previous result for methyl alcohol has been mentioned. T_1 for ethyl alcohol at 20°C has been measured as 2.2 seconds at 6,800 gauss and 1,100 gauss [9], and 3.5 seconds at 20°C at 1,650 gauss [8].

In order to obtain the self diffusion coefficient Δ the field gradients in the sample must be known and may be estimated from the echo width, however with some ambiguity since our field gradient was not linear but

simply the inhomogeneity encountered in the laboratory, of value about $100 \mu\text{G}/\text{cm}$. Hence our value of Δ for water at 25°C of $7 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ does not agree well with the known value, 2.1×10^{-5} [10]. We do however have a constant inhomogeneity and so can measure relative diffusion constants and in column [4] of the Table we give the values relative to

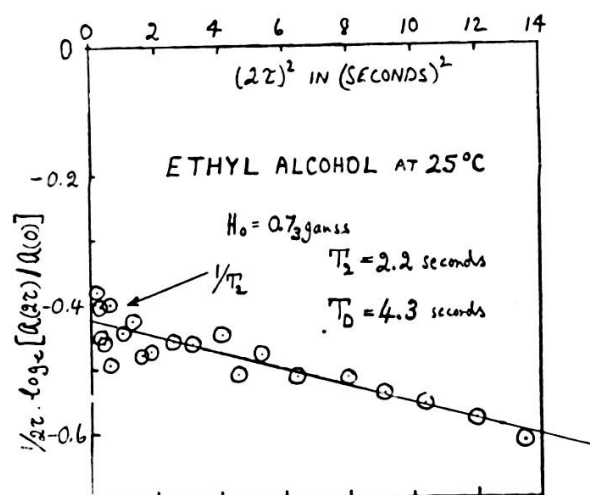


Fig. 3.

water. These may be compared with the values obtained by tracer methods (column 5) using porous barriers [11]. The difference is very striking especially for the higher alcohols, and while not claiming a very high accuracy for our measurements we do feel they throw some doubt on the measurements of self diffusion in these materials using porous barriers. It is perhaps significant that the tracer diffusion coefficients are smaller and it is known that the long chain acids have some tendency for the hydroxyl groups to stick to surfaces.

It is interesting to compare our T_2 measurements (T_1 for water and methyl alcohol are considered below) with the self diffusion coefficient Δ , which although we have measured it by using nuclear resonance is an independent parameter. We also consider the dielectric critical frequency ν (diel) [12]. The following approximate formulae may be considered in a qualitative analysis.

$$T_2 = \left(\frac{\sqrt{3} \cdot \pi^2}{2} \right) T_{2r}^2 \nu (\text{NMR}) \quad (1)$$

$$\Delta = \pi/6 \cdot a^2 \nu (\Delta) \quad (2)$$

$$\eta = S/2\pi \nu (\eta) \quad (3)$$

where T_{2r} is the "rigid lattice" relaxation time, a is an elementary molecular step and S is the shear modulus (Maxwell's relation).

From (1) and (2) we have $T_2/\Delta \propto \nu(\text{NMR})/\nu(\Delta)$. T_2/Δ is almost constant in column (8) of the Table showing a close relation between the motions causing nuclear relaxation and self diffusion. Again from (1) and (3) $T_2 \eta \propto \nu(\text{NMR})/\nu(\eta)$ which is shown in column (9) and the relation between T_2 and viscosity is evidently less simple. Finally $T_2/\nu(\text{diel}) \propto \nu(\text{NMR})/\nu(\text{diel})$ and as shown in column (10) there is little relation between nuclear relaxation and dipolar reorientation especially in the higher alcohols.

TABLE.

Liquid at 25° C	1	2	3	4	5	6	7	8	9	10
	$T_2 \pm 10\%$ sec	$T_1 \pm 10\%$ sec	$T_D^3 \pm 25\%$ sec ³	$\Delta/\Delta H_2 O$, this paper	$\Delta/\Delta H_2 O$ by tracer ¹⁰	$\nu_{\text{diel}} \times 10^{-9}$ c/s	η in cp	$T_2/(\Delta/\Delta H_2 O)_{\text{NMR}}$	$T_2 \eta$ in cp/sec	$T_2/\nu_{\text{diel}} \times 10^9$
H ₂ O	2.7	3.6	66	[1.0]	[1.0]	17	0.9	2.7	2.4	0.16
·										
·										
CH ₃ OH	2.5	(6 and 2)	69	0.9 ₆	0.94	2.3	0.55	2.6	1.4	1.1
C ₂ H ₅ OH	2.3	2.2	78	0.8 ₅	0.42	1.1 ₁	1.6	2.7	3.7	2.1
C ₃ H ₇ OH	1.9	2.0	103	0.6 ₅	0.27	0.30	2.0	2.9	3.8	6.3
C ₄ H ₉ OH	1.5	1.4	110	0.6 ₀	0.21	0.24	2.6	2.5	3.9	6.3
C ₅ H ₁₁ OH	1.1 ₅	1.0 ₅	(200)	—	—	—	4.3	—	5.0	—
·										
·										
C ₈ H ₁₇ OH	0.8	0.8 ₅	—	—	—	0.09	7.2	—	5.8	9.0

The motion which primarily determines the proton relaxation especially in the higher alcohols is that of the links of the carbon chain since this determines the motion of the CH₂ groups and so we suggest that the self diffusion coefficient is controlled by the motion of links rather than of the molecule as a whole, although these ideas merge for the lower alcohols.

The end of the chain, which carries the electric dipole, evidently reorients more slowly than the other parts of the molecule and one naturally thinks of restriction of motion by hydrogen bond association. This association need only be broken much less frequently than the mean time for reorientation of a link and so it is natural to expect ν (NMR)/ ν (diel) to increase with increasing chain length.

Water and methyl alcohol are exceptional in that T_1 is different from T_2 , and this will be discussed elsewhere together with other examples [13].

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ERRATUM

Owing to an error in calculation, it was stated that the T_1 decay curve for methyl alcohol was not of the expected form. In fact it (fig. 2) can be fitted to an expression of the form $M_z = \frac{3}{4} M_0 (1 - \exp - t/2.5) + \frac{1}{4} M_0 (1 - \exp - t/8.5)$. Hence $T_{1CH_3} = 2.5$ secs. and $T_{1OH} = 8.5$ secs. It is reasonable to find $T_{1OH} > T_{1CH_3}$ since the hydroxyl proton does not have near neighbours at a fixed distance.