^{13}C Relaxation Time Study of Hydrophobic Bonding

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Summary ^{13}C T_1 nuclear magnetic relaxation times have been measured for n-propanol and 2-n-butoxyethanol in a variety of solvents; the results show that water is exceptional in the extent to which it restricts solute molecular motion.

Because of sensitivity limitations, there have been few studies[1] of solvent effects on ^{13}C T_1 nuclear magnetic relaxation times. However, such studies are expected to yield new and detailed information about molecular motions in solution, because of their ability to distinguish the motions of different parts of a molecule. It is fairly well established[2] that the relaxation times of ^{13}C nuclei directly bonded to protons in medium-sized molecules are dominated by the time-dependence of the dipole coupling to these protons, so that, provided that the correlation time τ_c is much less than 1/Larmor frequency, then T_1 is proportional to $1/n\tau_c$, where n is the number of protons directly bonded to the ^{13}C nucleus under study. Thus relative ^{13}C T_1's for the same nucleus in various solvents are directly proportional to the mean extent of molecular motion.

n-Propanol and 2-n-butoxyethanol were selected for study because of their convenient solubilities in various solvents and because their alkyl and oxygen parts are thought to display typical hydrophobic and hydrophilic characteristics. The results are listed in the Table; the more important n-propanol results are the mean of between two and four measurements with good reproducibility (±5%) but the 2-n-butoxyethanol results are probably only ±10%. Care was taken to minimise r.f. inhomogeneity over the sample volume, and to ensure adequate relaxation between the 180°–τ–90° pulse sequences.[3] The resistivity of the water used was greater than 2 MΩcm^{-3}. Non-deuteriated samples were studied using a coaxial capillary ^{2}H lock, and all samples were deoxygenated by nitrogen. Measurements were carried out on a Bruker WH90 spectrometer at 22·62 MHz and at 304 K.

Table. ^{13}C Relaxation times at 304 K/s

Carbons in molecular order	Me[a]	CH_2	CH_2OH	Cyclohexane	Viscosity of pure solvent at 304 K/cp[b]
n-Propanol (pure)	8·3	5·4	5·0	—	1·67
+ 15% v.v. cyclohexane . .	8·4	5·5	5·1	17	—
15% v.v. in H_2O	8·6	7·3	7·7	—	0·78
in D_2O	7·3	6·1	6·1	—	0·95
in $CDCl_3$	12·2	10·8	10·5	—	0·45
in C_6D_6	11·8	10·0	8·9	—	0·46
in $(CD_3)_2SO$	9·9	9·4	8·2	—	1·79
Cyclohexane (pure)	—	—	—	21·3	0·81

Carbons in molecular order	Me[a]	CH_2	CH_2	CH_2—O—CH_2		CH_2OH
2-n-Butoxyethanol (pure) . .	5·1	4·5	3·5	3·3	2·3	2·1
20% v.v. in H_2O	5·3	4·4	3·0	3·0	2·6	2·5
in D_2O	4·7	3·7	2·9	2·2	2·0	2·3
in $(CD_3)_2SO$	5·3	4·9	3·4	2·4	2·7	4·0

[a] Actual T_1; should be multiplied by 1·5 for direct comparison with CH_2 groups. [b] 1 cp = 10^{-3}N s m^{-2}.

The general variation of relaxation times along the carbon chains in both alcohols studied is as expected; the usual enhanced mobility of the Me group is apparent. It is also expected to find an increase in the T_1's in solution at the hydroxy end of the chain, especially in n-propanol, since dilution in solvent would reduce inter-alcohol hydrogen-bonding. The non-aqueous T_1's show a modest viscosity dependence, although to a smaller extent than predicted.[4] The surprising observations are the comparatively short T_1's in aqueous solution. In D_2O especially, the n-propanol CH_2 T_1's are almost as short as in the neat alcohol, and the Me T_1 is shorter. On the basis of viscosity alone, by comparison with the C_6D_6 and the $(CD_3)_2SO$ results, the T_1's in D_2O should be about 10·8, 9·7 and 8·5 s. They are about two thirds of this, the effect being particularly apparent at the hydrophobic end of the alcohol. Thus the effect of H_2O and D_2O is to reduce the extent of solute molecular rotational motion by up to one third. This observation fits with an earlier study which showed that 10—25% n-propanol solutions in water have unexpectedly high viscosities.[5] The greater effect of D_2O is probably due to its greater viscosity, the effect being enhanced by the comparatively tight aqueous solvation of the n-propanol. It also underlines the generally agreed contention[2] that ^{13}C T_1's of carbon nuclei directly bonded to protons are relatively unaffected by more distant nuclei.

The 2-n-butoxyethanol results support the n-propanol results, although the effects noted above are slightly less marked, possibly because of the greater concentrations used. All the results are consistent with Levy's T_1 concentration study on phenol in H_2O, D_2O and $CDCl_3$.[1]

The cyclohexane results reveal a further feature of the structure of liquid n-propanol. Addition of 15% cyclohexane does not detectably affect the alcohol T_1's, and has only a moderate effect on the cyclohexane T_1. This is consistent with the alcohol molecules being linked at their hydroxy ends, leaving hydrophobic regions of reduced microviscosity.

Nearly all current theories of hydrophobic bonding make the assumption that the transfer of a solute molecule into water, from the gas phase or from a non-aqueous solvent, has no significant effect on the motions of the solute molecule.[6] Thus the observed entropy decrease for such processes is attributed entirely to solute-induced changes in water structure. The present results suggest that at least some of this entropy decrease comes from a restriction of the solute molecular motions, which could simply be due to the unusually high internal pressure of water and to its effectiveness in packing tightly around hydrophobic solutes.

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[1] G. C. Levy, *J. Magn. Res.*, 1972, **8**, 122; J. D. Cargioli and F. A. L. Anet, *J. Amer. Chem. Soc.*, 1972, **95**, 1527.

[2] (a) T. D. Alger and D. M. Grant, *J. Phys. Chem.*, 1971, **75**, 2539; (b) G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley-Interscience, New York, 1972, p. 179.

[3] R. Freeman and H. D. W. Hill, *J. Phys. Chem.*, 1971, **54**, 3367.

[4] Ref. 2(b), p. 202.

[5] S. Z. Mikhail and W. R. Kimel, *J. Chem. and Eng. Data*, 1963, **8**, 323.

[6] See R. H. Aranow and L. Witten, *J. Phys. Chem.*, 1960, **64**, 1643, for an exception.