Solvent Isotope Shifts of Caesium Resonances in Dilute Salt Solutions

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DURING studies of chemical shifts of caesium nuclear resonance in dilute solutions of caesium salts in water and in nonaqueous solvents, we studied the effects of changing the isotopic composition of the solvent. The results throw new light on the mechanism of the isotope effect in these solutions.

The solvent isotope shift of the caesium resonance in 0·5 M- and 1·0 M-CsCl solutions in $H_2^{16}O$, D_2O, and $H_2^{18}O$ has already been recorded[1] and interpreted in terms of changes in the molecular vibration amplitudes of the ion–solvent complex. Our new measurements are of greater precision and extend the concentration range to as low as 0·005M.

Figure 1 shows the frequency of the Cs resonance near 28·013 MHz. at fixed applied field as a function of molar
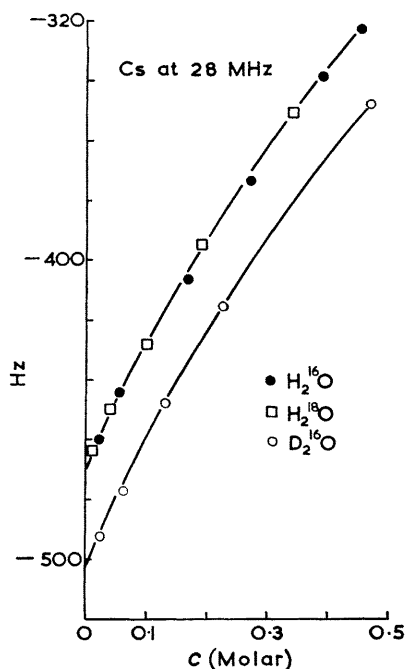

FIGURE 1

concentration in $H_2^{16}O$, $D_2^{16}O$, and $H_2^{18}O$. The shifts in $H_2^{16}O$ and $H_2^{18}O$ are indistinguishable and extrapolate to the same value at infinite dilution, whereas the shift at infinite dilution in $D_2^{16}O$ lies at a lower value (a diamagnetic shift). Since the masses of $H_2^{18}O$ and $D_2^{16}O$ are the same, though the infinite dilution shifts are different, and also because the masses of the $H_2^{16}O$ and $H_2^{18}O$ are different but the shifts are the same, the isotope effects cannot simply be a function of the masses of the molecules. These results suggest strongly that at infinite dilution the isotope effect is caused by a change of the strength of the solvent hydrogen bonds in passing from H_2O to D_2O. The paramagnetic shift of the Cs resonance caused by adjacent water molecules arises mainly from "overlap" interactions[2] and these will depend
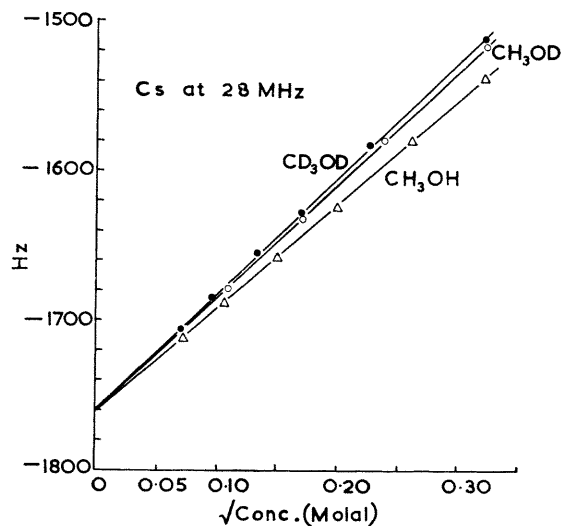
on the distance of closest approach and on the orientation of the water molecules. The somewhat stronger hydrogen bonds formed by D_2O compared with H_2O might easily modify the parameters so as to cause the observed diamagnetic shift.

By contrast with the low concentrations, the shifts at high concentrations all converge at *ca.* 4M. The effect is difficult to display on a small graph because of the precision of the measurements. The convergence is shown in a selection of results in the Table. These results were interpolated from 23 solutions of different concentrations in $H_2^{16}O$, 18 solutions in D_2O, and 10 solutions in $H_2^{18}O$. This behaviour is consistent with the hypothesis that changes of hydrogen bonding are responsible for the shifts. Caesium is a structure-breaking ion and at high concentrations the effect of

FIGURE 2

TABLE

Chemical shifts of Cs *resonance at* 28·013 MHz. *with reference to* 1·994-*molal* CsCl *in* H_2O

Molar concentration	Cs+ in H_2O (Hz.)	Cs+ in D_2O (Hz.)	Shift difference (Hz.)
0·100	−428	−461	33
0·200	−395	−425	30
0·400	−335·8	−367·6	32
0·900	−211·3	−235	24
1·10	−165·5	−185·6	20
2·20	+ 79·3	+ 62·5	17
2·60	168·3	157·5	11
3·00	258·4	252·5	6
4·00	493	493	0
6·00	1012	1012	0

hydrogen bonding in the water is greatly reduced, with a consequent increase in the shift in D_2O solutions; the isotope effect is destroyed with the breaking up of the water structure.

The effect on the chemical shift of Cs+ in methanol and

deuteriated methanol was also measured. Figure 2 shows the chemical shift of the Cs resonance as a function of (concentration)$^{\frac{1}{3}}$. This plot is linear for reasons to be given in a forthcoming publication.[3] At concentrations near 0·1M there is a small isotope effect in the different solvents, but the shifts at infinite dilution are all the same, within experimental error.

The measurements were made using a superconducting magnet operating at *ca.* 50 kgauss (5T).[4] Shifts could be reproduced with a precision of ± 1·5 Hz. at 28 MHz. The samples were contained in spherical bulbs of 9 mm. diam. and resonances were recorded with respect to an external standard of 1·994 M-CsCl–H_2O. The temperature was controlled to 25 ± 0·1°.

[1] A. Loewenstein, M. Shporer, P. C. Lauterbur, and J. E. Ramirez, *Chem. Comm.*, 1968, 214.
[2] J. Konobo and J. Yamashita, *J. Phys. Chem. Solids*, 1959, **10**, 245; D. I. Kenberry and T. O. Das, *J. Chem. Phys.*, 1965, **138**, *A*, 822.
[3] J. Halliday, R. Sharp, and R. E. Richards, to be published.
[4] J. Halliday, H. D. W. Hill, and R. E. Richards, *J. Sci. Instr.*, in the press.