Direct Detection of Anion Shifts in the Hydroxyl Proton Resonance Spectrum of Methanol

By R. N. BUTLER, Miss E. A. PHILLPOTT, and M. C. R. SYMONS*
(*Chemistry Department, The University, Leicester*)

SINCE the discovery of a separate resonance signal from solvent molecules directly bonded to cations in certain solvents at low temperatures,[1] attention has been paid to such factors as the solvation number of the cation and to the rate of exchange of bound with bulk solvent.[2] This has perhaps obscured the fact that the residual shift of the main solvent signal from that of pure solvent (*e.g.* cd in Figure) is caused largely or even completely by the rapid exchange between bulk solvent molecules and those bonded to the anions. The Figure depicts diagramatically the type of spectrum observed and the hypothetical resonances involved when the electrolyte is magnesium perchlorate and the solvent methanol.

In most studies of the effect of electrolytes on the n.m.r. spectra of solvents[3] attempts are made to divide the total molal shift† into individual contributions from cations and anions, but these are inevitably arbitrary and need not be even approximately correct. Our direct measurement shows that for magnesium perchlorate in methanol the molal anion shift is about one third that of the cation and operates in the opposite direction

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† The molal shift represents the limiting value of the characteristic chemical shift for a given salt in dilute solution $(\mathrm{d}\delta/\mathrm{d}c)_{c=0}$. The total salt shift is related to the molal shifts of the cation and anion by the equation

$$\delta_{\mathrm{obs}} = m(n^{+}\delta^{+} + n^{-}\delta^{-})$$

where m is the salt concentration, n^{+} and n^{-} are the number of moles of cation and anion formed in the dissociation of one mole of salt, and δ^{+} and δ^{-} are the molal shifts of the individual cation and anion.

(Table). Both cation and anion shifts, measured in the range −65° to −30°, were independent of temperature. The anion shifts were measured directly and the cation shifts were determined as the weighted mean of the resonances a and c from the known concentrations of bound and bulk solvent.[1,2] The overall salt shifts, measured above the coalescence point in the range 40° to 10°, were also almost independent of temperature. Each of the shifts was linearly dependent on concentration up to about 0·6 molal, at which point both the salt and anion shifts deviated from the linear relationship.

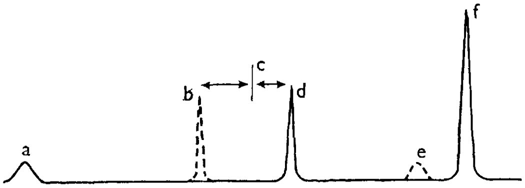

FIGURE. *Low-temperature* ^1H n.m.r. *resonances of magnesium perchlorate–methanol solutions*

(a) OH of cation solvation shell.

(b) Hypothetical OH after coalescence of the signals from the cation solvation shell and pure methanol.

(c) OH of pure methanol. The shift bc is due to the cation.

(d) Observed OH of magnesium perchlorate–methanol solution, resulting from coalescence of the signals from bulk solvent molecules and those bonded to the anions. The shift cd is due to the anion and minor modifications of solvent intermolecular structure.

(e) Hypothetical anion solvation shell.

(f) Me of bound and bulk solvent.

TABLE

Separate ion shifts[a] *in the hydroxyl proton resonance of methanol in magnesium perchlorate–methanol solutions*

Molality	Anion shift (×2)	Cation shift[b]	Salt shift calc.	Salt shift obs.
0·470	4	−9	−5	−6
0·236	2	−4·5	−2·5	−3
0·121	1	−3	−2	−1·5

[a] Shifts are given in c./sec. and were measured on a Varian A60 n.m.r. spectrometer with a Varian V-6040 n.m.r. Variable Temperature Control. The methanol Me-signal was used as reference. A small shift was noted in this signal with increasing concentration of salt and the data are corrected for this.

[b] Shifts downfield are regarded as negative and those upfield as positive.

From these measurements extrapolated through the coalescence point we are in a position to measure the molal shifts for a range of cations and anions.

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