# Carbon-13 Nuclear Magnetic Resonance as a Tool to study Organic Solvation Shells

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*Summary* Two $^{13}C$ n.m.r. signals, one for the bulk and one for the bound solvent (1·94 p.p.m. upfield) are observed for aqueous dimethyl sulphoxide containing aluminium chloride.

IT is well known that n.m.r. spectroscopy may be used to study solvation shells, since solvent molecules directly bound to a metal cation have different chemical shifts from those of the bulk solvent.[1] A great variety of nuclei have been used for this purpose: $^{1}H$, $^{17}O$, $^{31}P$, $^{27}Al$, $^{69}Ga$.[1] At the present time, it seems that nobody has explored the possibility of using $^{13}C$ n.m.r. ("C.m.r.") on non-enriched samples. We report here a preliminary experiment showing the potential of this $^{13}C$ method.

Using a solution of aluminium chloride in a mixture of dimethyl sulphoxide and water, already studied by means of $^{1}H$ n.m.r. by Fratiello and Schuster[2] and Thomas and Reynolds[3] in their pioneering work, we obtained two $^{13}C$ signals (Figure) at 22·63 MHz with complete proton heteronuclear decoupling and Fourier transform accumulation (1000 scans). $^{1}H$ and $^{13}C$ spectra are displayed side by side in the Figure to show the similarity of the $Me_2SO$ solvation numbers obtained from the relative areas of the two signals: 1·08 (Figure a) and 0·24 (Figure b). Two different concentrations have been used so as to identify bulk and bound solvents unequivocally.

As for $^{31}P$,[1c,4] the bound $^{13}C$ signal appears upfield, with a chemical shift far larger than for $^{1}H$: $-44$ Hz or $-1·94$ p.p.m., against $+13$ Hz (at 60 MHz) or $+0·21$ p.p.m. The carbon atom of $Me_2SO$ is indeed one link closer to the aluminium cation (presumably solvated to oxygen); moreover, $^{13}C$ chemical shifts are intrinsically larger than those of protons. The experiments were performed at 30°: the rather broad bound signal encourages us to hope that it might give rise to separate components at low temperature for the various solvates $[Al(Me_2SO)_i(H_2O)_{6-i}]^{3+}$, where $i = 1$—6, as with $^{31}P$ n.m.r. spectroscopy for analogous solutions of $AlCl_3$ in aqueous hexamethylphosphorotriamide.[4]

These experiments may open a new route to solvation studies in organic solvents, especially with amides, nitriles, and ketones, for which the solvated carbon atom is very close to the cation.

$^{13}C$ spectra at 22·63 MHz were kindly supplied by Brüker Society, Karlsruhe (Germany), operating with a HX 90/2 apparatus, equipped with Fourier transform set and wide-band proton decoupling.

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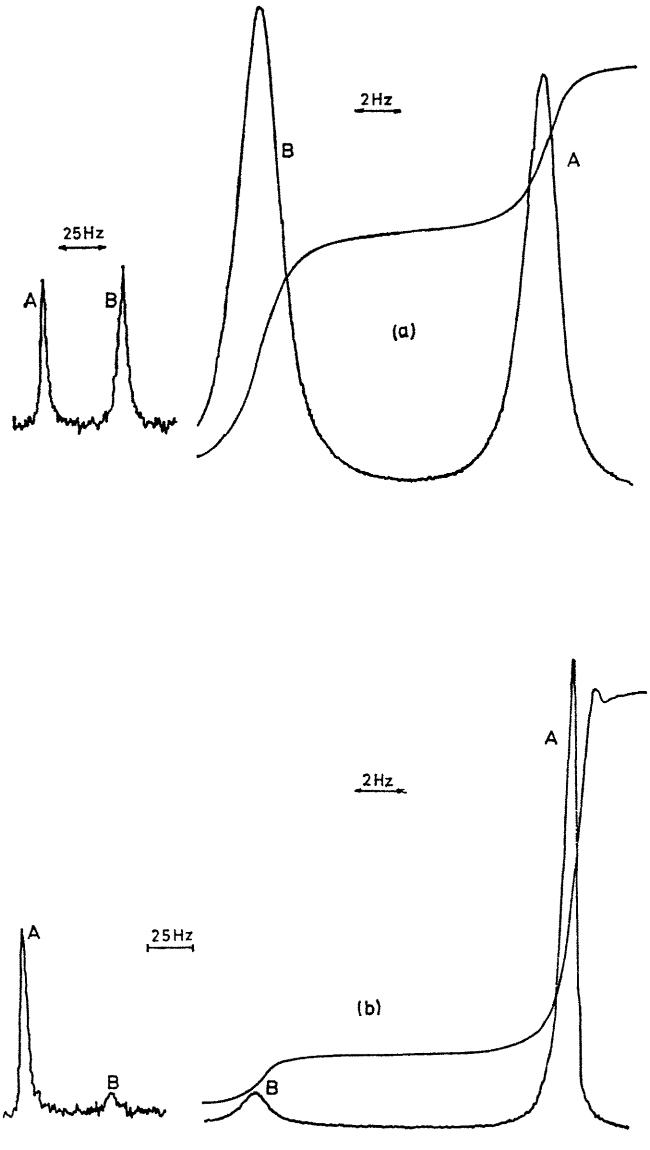

FIGURE. $^{1}H$ *and* $^{13}C$ *spectra* (*right and left, respectively*) *for* $D_2O$ *solution of* $AlCl_3$ *in* $Me_2SO$ *for a molar ratio* $[AlCl_3]/[Me_2SO] = 0·545$ *and* $Me_2SO$ *solvation numbers*: 1·08 (a) *and* 0·24 (*by diluting the previous solution with* $D_2O$; (b). *Free solvent*: A; *bound solvent*: B.

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[1] For a review, see:
(a) J. F. Hinton and E. S. Amis, *Chem. Rev.*, 1967, **67**, 367; (b) C. Deverell, *Prog. N.M.R. Spectroscopy*, 1968, **4**, 235; (c) J. J. Delpuech, A. Peguy, and M. R. Khaddar, *J. Electroanalyt. Chem.*, 1971, **29**, 31, and refs. therein.

[2] A. Fratiello and R. Schuster, *Tetrahedron Letters*, 1967, 4641.

[3] S. Thomas and W. L. Reynolds, *J. Chem. Phys.*, 1966, **44**, 3148.

[4] J. J. Delpuech, A. Peguy, and M. R. Khaddar, *J. Magnetic Resonance*, in the press.